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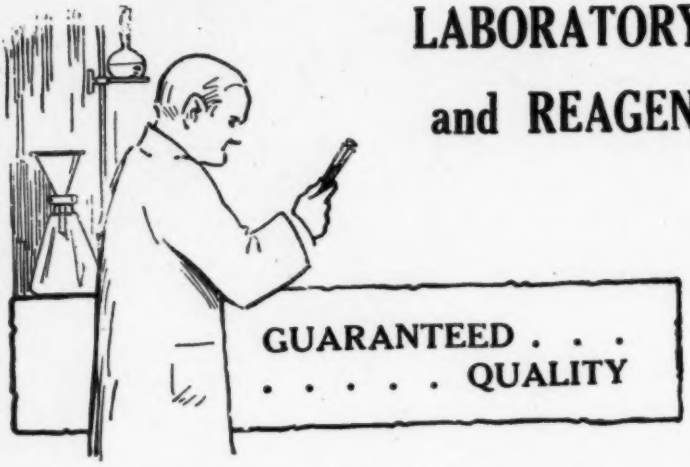

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333	Table I, column 6, line 5	C, 66.51	61.51
491	Abstract, line 6	Beer's law between 4 and 150	Beer's law between 1 and 150
493	1	"A saturated aqueous solution" etc.	"A 0.2% aqueous solution" etc.
,,	8	(0.02 mg. to 7.5 mg. etc.)	(0.05 mg. etc.)
585	Equation	$\frac{[P]}{[R] \times (\log_{10}[P] - \log_{10}[R])}$	
601	3	$\frac{1}{\xi_a} = \frac{1}{\xi} + \frac{m}{r}$	$\frac{1}{\xi_a} - \frac{1}{\xi} + \frac{m}{r}$
602	15	π	σ
,,	25	1940	1040
604	11	$a < 1 \ldots a^4$	$a > 1 \ldots a_4$
	25	(Vide Table I)	(Vide Table II)
	26	π	λ
605	Table I	Asterisk (*) to precede $\xi_a = \frac{Hk}{P}$ etc.	

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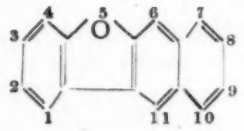
[Jour. Indian Chem. Soc., Vol. 30, No. 1, 1953]

EXPERIMENTS ON THE SYNTHESES OF FURANO COMPOUNDS. PART I. A NOVEL ROUTE TO β-BRAZANS*

By J. N. Chatterjea

An unambiguous synthesis of Kostacecki's 3 : 8 : 9-trimethoxy-β-brazan has been achieved by the cyclodehydration of 6-methoxy-3-(3 : 4-dimethoxybenzyl)-2-formylcoumarone obtained by the Gattermann reaction on 6-methoxy-3-(3 : 4-dimethoxybenzyl)-coumarone which has been synthesised in two different ways. The Hoesch reaction on the latter is shown to give 2-acyl derivative. The cyclisations of a few 2-acyl-3-benzylcoumarones have been studied.

β-Brazan (I) (phenylene-ββ-naphthylene oxide) is known to accompany 1 : 2-benznaphthacene in the coal-tar distillate (Fieser, "Chemistry of natural products related to phenanthrene", Reinhold Publishing Corp., 1937, p. 20). An important derivative of this substance is 3 : 8 : 9-trimethoxy-β-brazan (IV, R = H) obtained from the natural product brazilin (a pyrane compound). By heating O-trimethylbrazilone (II) with hydriodic acid for a long period, Kostanecki and Lloyd (*Ber.*, 1903, **36**, 2198) obtained 3 : 8 : 9-trihydroxy-β-brazan which gave the trimethyl ether (IV, R = H) (m. p. 244-46°) on methylation. In this reaction, the diketone (II) undergoes a remakable rearrangement to the coumarone derivative (III)



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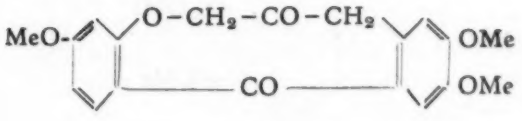

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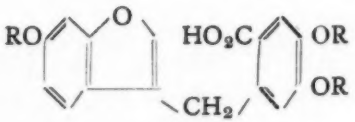

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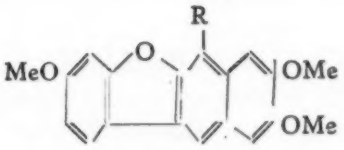


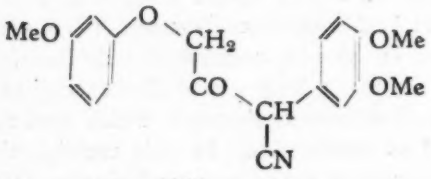
(IV)

which then cyclises to 3 : 6 : 8 : 9-tetrahydroxy-β-brazan (IV, R = OH and and OH in place of OMe). The latter is reduced by a further action of hydriodic acid to 3 : 8 : 9-trihydroxy-β-brazan the constitution of which has been confirmed by converting the hyd oxybrazan into β-brazan (I) with the aid of zinc dust (cf. Perkin and Robinson, *J. Chem. Soc.*, 1909, **95**, 386). Although a number of syntheses of β-brazan are known (Kostanecki and Lampe, *Ber.*, 1908, **41**, 2373 ; Mosettig and Robinson, *J. Amer. Chem. Soc.*, 1939, **61**, 1149 ; Orchin and Reggel, *ibid.*, 1948, **70**, 1245 ; cf. Ebel, *Helv. Chem. Acta*, 1929, **12**, 3), the methods are by no means

*A preliminary account of a part of the work appeared in *Experientia*, 1951, **7**, 374.

general and universally applicable. The present communication deals with an unambiguous and general method for the synthesis of 3 : 8 : 9-trimethoxy-β-brazan and some of its derivatives.

The keto-nitrile (V) of Pfeiffer *et al.* (*Ber.*, 1930, **63**, 1304), obtained by the condensation of ethyl *m*-methoxyphenoxyacetate with homoveratronitrile, gives the amide (VI) with fuming hydrochloric acid in acetic acid at the room temperature (15°-18°). At the higher temperature (30°), the sole crystalline product, however, was the cyclised amide (VII). This on prolonged boiling with 10% hydrochloric acid afforded 6-methoxy-3-(3 : 4-dimethoxybenzyl)coumarone (VIII, R = H) (isolated through the picrate) with the loss of the amide group by hydrolysis and decarboxylation. The constitution of this compound was confirmed by obtaining it from 5-methoxy-2-(3 : 4-dimethoxyphenylacetyl)phenoxyacetic acid (IX) (Bentley and Robinson, *J. Chem. Soc.*, 1950, 1355) by the action of sodium acetate and hot



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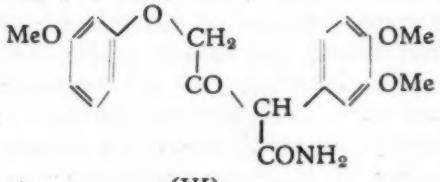

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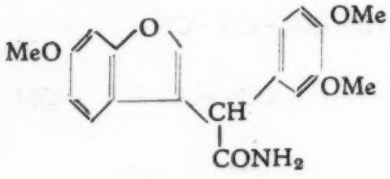

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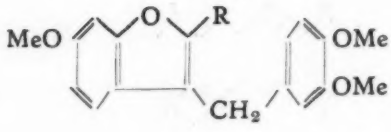

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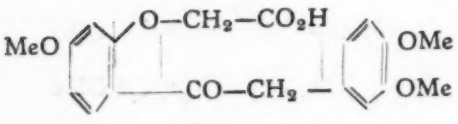

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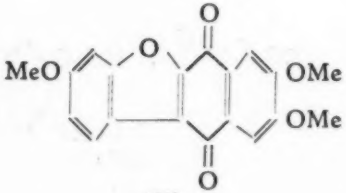


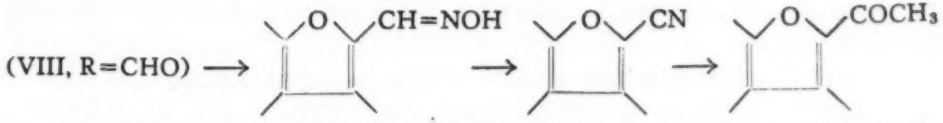
(X)

acetic anhydride. On Gattermann synthesis with hydrogen cyanide and zinc chloride, (VIII, R = H) furnished the aldehyde (VIII, R = CHO) the orientation of which was established by oxidising it with potassium permanganate in acetone to the known acid (VIII, R = CO_2H) obtained by Bentley and Robinson (*loc. cit.*) by the cyclisation of the phenoxyacetic acid (IX) with sodium ethoxide. The aldehyde (VIII, R = CHO) underwent quantitative Bergmann cyclisation* on short

* This type of cyclisation was first observed by Bergmann (*J. Org. Chem.*, 1939, 4, 1) who obtained anthracene as one of the products of hydrolysis of the acetal of *o*-benzylbenzaldehyde.

treatment with glacial phosphoric acid at 100° giving the β-brazan (IV, R=H) (m. p. 244-46°). Although the synthetic product was not compared with that from the natural sources, the correctness of the synthesis was confirmed by typical reactions (cf. *Ber.*, 1903, **36**, 2198) and by oxidising it with chromic acid to the known trimethoxybrazanquinone (X) (m. p. 261-62°), obtained by Kostanecki and Lloyd in a different way (*Ber.*, 1903, **36**, 2200).

The Hoesch reaction with the coumarones does not appear to have been studied in detail. Karrer *et al.* (*Helv. Chim. Acta*, 1919, **2**, 454; 1920, **3**, 541; 1921, **4**, 718) had obtained 5-acyl or aroyl derivatives by the Hoesch reaction with 6-hydroxy-3-methylcoumarone*. In the present case, however, the coumarone (VIII, R=H) gave with acetonitrile and zinc chloride the 2-aceto compound (VIII, R=COMe). The orientation of this compound was established by preparing it in the following way :



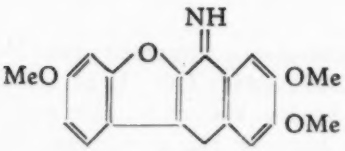
The oxime of the aldehyde (VIII, R=CHO) on dehydration with acetic anhydride furnished the nitrile (VIII, R=CN) which with methylmagnesium iodide gave the ketone (VIII, R=COMe) identical with the Hoesch condensation product. Attempts to obtain this ketone by the action of diazomethane on the aldehyde (VIII, R=CHO) were unsuccessful; while intractable tar was obtained by the action of acetic anhydride and stannic chloride on (VIII, R=H) (cf. Smith's method of acylation of coumarones, *Chem. Abs.*, 1938, **32**, 2938). An attempt to cyclise the nitrile by internal Hoesch reaction so as to obtain (XI) was also unsuccessful.

The syntheses of 2-propionyl, 2-*n*-butyryl, 2-*iso*butyryl derivatives of the coumarone were similarly done by the action of appropriate Grignard's reagent on the nitrile (VIII, R=CN).

A purely qualitative study on the case of cyclisation of the various acyl derivatives (VIII, R=CHO or COMe etc.) showed that while the aldehyde (VIII, R=CHO) cyclised with glacial phosphoric acid at 100° during 10 minutes, the acetyl compound (VIII, R=COMe) did so during one and half hours and the propionyl compound (VIII, R=COEt) cyclised only at a higher temperature (180°-185°). The *n*-butyryl compound (VIII, R=COPr) and the *iso*butyryl compound [VIII, R=COCH$(CH_3)_2$] did not cyclise even at higher temperatures, instead these showed signs of decomposition. The ease of cyclisation is thus dependent on the nature of groups attached to the carbonyl group, the relative order being $H > CH_3 > C_2H_5 > \begin{matrix} C_3H_7\ (n) \\ C_3H_7\ (iso) \end{matrix}$ which is in the increasing order of +I effect. The result falls in line with the observations by Berliner (*J. Amer. Chem. Soc.*, 1944, **66**, 533) who found a similar order in the rate constants in the cyclisations of various

* Robertson *et al.* (*J. Chem. Soc.*, 1949, 2057) have proved that Karrer's were really 2-acyl coumarone.

alkyl ketones having similar strcutural features. Berliner found an explanation for the decrease in the rate of cyclisation with increasing length of the alkyl chain in terms of the increasing electron releasing character of the alkyl group. The electron



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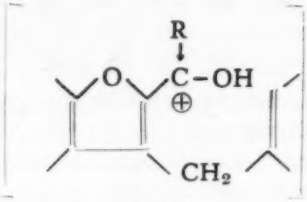

(XII)

release increases the electron density of the positively charged central carbon atom of the conjugate acid (XII) (which is the intermediate in the process of cyclisation) decreasing the effective positive character and therefore a decrease in the rate results.

It is proposed to extend this synthesis of β-brazans to other cases.

EXPERIMENTAL

(All m.p.'s are uncor.)

Keto-nitrile (V) was prepared according to Pfeiffer *et al.* (*loc. cit.*) by the condensation of ethyl *m*-methoxyphenoxyacetate and homoveratronitrile in the presence of alcoholic sodium ethoxide. The product was freed from oily impurities by pressing over a porous pot and crystallised from acetic acid, as hard prisms, m. p. 92-94° (lit. m. p., 95°). (Found : C, 67.0 ; H, 5.8. Calc. for $C_{19}H_{19}O_5N$: C, 66.8 ; H, 5.6 per cent).

6-*Methoxy*-3-[α-(3 : 4-*dimethoxyphenylacetamido*)]*coumarone* (VII).—A solution of the foregoing keto-nitrile (24.0g.) in acetic acid (350 c.c.) was treated at the room temperature with fuming hydrochloric acid (250 c. c., sat. at 0°). The mixture was well corked and maintained at 30° for 24 hours. The brown solution was added to a large volume of water and the precipitate (24 g.) collected after 24 hours, dried and crystallised from alcohol. The *coumarone* was obtained in colorless, flat needles (11. 5 g.), m. p. 162°. (Found : C, 67.1 ; H, 5.8. $C_{19}H_{19}O_5N$ requires C, 66.8 ; H, 5.6 per cent). The compound gives no coloration with alcoholic ferric chloride.

6-*Methoxy*-3-(3 : 4-*dimethoxybenzyl*)*coumarone* (VIII, R = H). *Method* (*a*).—The above amide (5.0 g.) was boiled under reflux with hydrochloric acid (10%, 140 c.c.) for 6 hours when the solid gradually became completely oily. The mixture was cooled, extracted with ether (2×40 c. c.) and the product treated with a strong solution of alcoholic picric acid. The picrate of the coumarone (VIII, R = H) (5.4 g.) was collected and crystallised from dilute alcohol in fine, orange needles, m. p. 102°. (Found : N, 7.6. $C_{18}H_{18}O_4$. $C_6H_3O_7N_3$ requires N, 8.0 per cent).

It was obtained quantitatively from the picrate by washing an ethereal suspension of the picrate several times with dilute sodium hydroxide. On removal of ether, an oil was obtained which quickly solidified. The product crystallised from methanol in colorless needles, m. p. 61-62°. (Found : C, 72.2, 72.4 ; H, 6.6, 6.2. $C_{18}H_{18}O_4$ requires C, 72.5 ; H, 6.4 per cent). It gives no colour reaction with ferric chloride. It gives a red coloration with sulphuric acid. The compound is easily soluble in all organic solvents.

Method (*b*). *From* 5-*Methoxy*-2-(3 : 4-*dimethoxyphenylacetyl*)*phenoxyacetic Acid* (IX) (cf. *J. Chem. Soc.*, 1950, 1355).—The above mentioned acid was conveniently prepared as follows : A mixture of 2-hydroxy-4-methoxyphenyl-3' : 4'-dimethoxybenzyl ketone (5 g.), ethyl bromoacetate (3.5 c. c.), potassium carbonate (15 g.) and acetone (50 c. c.) was heated under reflux for 6 hours. On removal of acetone, ethyl 5-methoxy-2-(3 : 4-dimethoxyphenylacetyl)phenoxyacetate was obtained as a non-crystallisable gum. This ester was hydrolysed by boiling under reflux for ½ hour with a solution of potassium hydroxide (6.0 g.) in alcohol (30 c. c.) containing water (10 c. c.). After removing alcohol in vacuum, the residue was diluted with water (80 c. c.) and 5-methoxy-2-(3 : 4-dimethoxyphenylacetyl)phenoxyacetic acid precipitated with dilute hydrochloric acid. Crystallised from glacial acetic acid, it was obtained in colorless needles (2.3 g.), m. p. 143°. (Found : C, 63.0 ; H, 5.7. Calc. for $C_{19}H_{20}O_7$: C, 63.3 ; H, 5.6 per cent).

A mixture of this phenoxy-acid (IX, 1.0g.), anhydrous sodium acetate (1.0 g.) and acetic anhydride (10 c. c.) was heated at 160° (oil-bath) for ½ hour and then poured into water. The gummy material was isolated by extraction with ether and then treated with alcoholic picric acid when the picrate (0.8g.) of (VIII, R = H) was obtained crystallising from alcohol in orange needles, m. p. and mixed m. p. 102°.

6-*Methoxy*-3-(3 : 4-*dimethoxybenzyl*)-2-*formylcoumarone* (VIII, R = CHO).—A solution of the coumarone (VIII, R = H) (1.0g.) and anhydrous hydrogen cyanide (1.5 c. c.) in ether (50 c. c.) containing zinc chloride (0.4g.) was saturated with hydrogen chloride at 0°. The crystalline aldimine hydrochloride appeared in course of ½ hour. Next day, the greenish product was washed twice with dry ether, treated with water and heated on the water-bath for ½ hour. The oily material that had first appeared was quickly replaced by a crystalline mass which was collected (1.0 g.) and obtained from alcohol in yellowish clusters of hexagonal plates, m.p. 137°. (Found : C, 69.7 ; H, 5.5. $C_{19}H_{18}O_5$ requires C, 69.9 ; H, 5.5 per cent). On being diluted with water the red solution of this compound in sulphuric acid became green and then blue.

The 2 : 4-*dinitrophenylhydrazone* separated from ethyl acetate in orange-red microcrystalline powder, m. p. 246-48°. (Found : N, 10.9. $C_{25}H_{22}O_8N_4$ requires N, 11.7 per cent).

The *semicarbazone* crystallised from alcohol in yellowish plates, m. p. 166-67°. (Found : N, 10.3. $C_{20}H_{21}O_5N_3$ requires N, 11.0 per cent). With sulphuric acid

the compound gives a yellow coloration ; on addition of water this turns green and then a red precipitate is obtained. Addition of alkali destroys this red colour which may be regenerated on acidification.

The *oxime* was prepared by heating the aldehyde (VIII, R = CHO) (4. 0 g.) in pyridine (10 c. c.) with hydroxylamine hydrochloride (3 g.) on the water-bath for 2 hours. It crystallsed from aqueous alcohol in colorless needles, m. p. 145-45.5°, yield 3.9 g. (Found : N, 3.9. $C_{19}H_{19}O_5N$ requires N, 4.1 per cent).

6-*Methoxy*-3-(3 : 4-*dimethoxybenzyl*)*coumarilic Acid* (VIII, R = CO_2H).—A solution of $KMnO_4$ (1.0 g.) in water (20 c. c.) was gradually added to the above-mentioned aldehyde (0.41 g.) in acetone (20 c. c.) at 50° during 1 hour. The mixture was cooled, cleaned by passing sulphur dioxide into the solution and then diluted with water (100 c. c.). The colorless crystalline precipitate (0.28 g.) of the coumarilic acid was collected and crystallised from acetic acid in colorless, slender needles, m. p. 196° (lit., 196.5°). (Found : C, 66.8 ; H, 5.4. Calc. for $C_{19}H_{18}O_6$: C, 66.6 ; H, 5.3 per cent). With a view to preparing the 6-nitro derivative of this compound (nitration in the veratrole nucleus), experiments on nitration were undertaken when an unidentified product was obtained as follows : A solution of the coumarilic acid (0.4 g.) was gradually treated at the room temperature with a mixture of nitric acid (0.3 c. c.), acetic acid (0.2 c. c.) and sulphuric acid (0.1 c. c.). The solution at once turned yellow and gradually a yellow crystalline solid appeared. The product was collected after 1½ hours and crystallised from acetic acid and obtained in yellow flakes, m. p. 182-84°. (Found : C, 54.8 ; H, 5.1%). The product is insoluble in alkali.

3 : 8 : 9-*Trimethoxy-β-brazan* (IV, R = H).—6-Methoxy-3-(3 : 4-dimethoxybenzyl)-2-formylcoumarone (1.0 g.) was suspended in glacial phosphoric acid (25 c. c.) and the mixture maintained at 100° for about 10 minutes. At first a greenish jelly was obtained which afterwards turned greyish white. The product was heated with water (100 c. c.) for a few minutes on the water-bath and the colorless product collected and washed thoroughly with water and alcohol. The compound crystallised from benzene in colorless, thick plates, m. p. 244-46° (Kostanecki, m. p. 244-46°), yield 0.9 g. (Found : C, 73.9 ; H, 5.2. Calc. for $C_{19}H_{16}O_4$: C, 74.0 ; H, 5.2 per cent). The compound is sparingly soluble in acetic acid and alcohol. With sulphuric acid the coloration is at first deep blue and then violet and finally turns green on keeping (in agreement with Kostanecki).

Trimethoxy-β-brazanquinone (X) (cf. *J. Amer. Chem. Soc.*, 1939, **61**, 1150).—A solution of the above brazan (0.4 g.) in acetic acid (12 c. c.) was treated gradually at the boiling point with a solution of chromic acid (1.0 g.) in a mixture of acetic acid (8 c. c.) and water (1 c. c.). After boiling for 10 minutes, the solution was cooled and water added to precipitate the quinone. The crude product (0.2 g.) was collected and trimethoxy-β-brazanquinone was obtained from acetic acid in fine, orange-red needles, m. p. 260-62°. The product may be further

purified and obtained in bright, orange-red, pointed needles, m. p. 261-62° by sublimation at 200° in vacuum (1 mm.), yield 0.05 g. (Found : C, 67.2 ; H, 4.3. Calc. for $C_{19}H_{14}O_6$: C, 67.5 ; H, 4.1 per cent). The compound is reduced by warm alkaline sodium hydrosulphite to a yellow solution. On addition of sulphuric acid, the compound gives a brownish solution having a violet tinge and on keeping the solution turns green.

6-*Methoxy*-3-(3 : 4-*dimethoxybenzyl*)-2-*acetocoumarone* (VIII, R=COMe).—A solution of the coumarone (VIII, R=H) (0.5 g.) in ether (30 c. c.) containing zinc chloride (0.3 g.) was treated with acetonitrile (1 c. c.) and saturated at 0° with dry hydrogen chloride. The solution was allowed to stay in the refrigerator and after 6 days the green solid was washed with dry ether and then heated with water (50 c. c.) on the water-bath. The crystalline mass (0.15 g.) of the product separated from alcohol in colorless, pointed plates, m. p. 156-57°. (Found : C, 70.3 ; H, 6.1. $C_{20}H_{20}O_5$ requires C, 70.6 ; H, 5.9 per cent). The yield of the product does not improve if anhydrous aluminium chloride be used along with zinc chloride as a catalyst. The red solution of the compound in sulphuric acid turns gradually green and then finally blue.

The 2 : 4-*dinitrophenylhydrazone* crystallised from nitrobenzene-alcohol in deep orange-red plates, m. p. 227°. (Found : N, 10.6. $C_{26}H_{24}O_8N_4$ requires N, 10.8 per cent).

The *oxime* (prepared in pyridine) crystallised from methanol in colorless needles, m. p. 131-32°. (Found : N, 3.6. $C_{20}H_{21}O_5N$ requires N, 4.0 per cent).

6-*Methoxy*-3-(3 : 4-*dimethoxybenzyl*)-2-*cyanocoumarone* (VIII, R=CN).—A solution of the oxime of (VIII, R=CHO, mentioned above) (4.0g.) in acetic anhydride (8 c. c.) was heated under reflux for ½ hour and then poured into water. The gummy solid was crystallised from alcohol and the compound was obtained in cream-colored flat needles, m. p. 130-31°, yield 2.4 g. (Found : C, 69. 8, 69.9 ; H, 5.3, 5.4. $C_{19}H_{17}O_4N$ requires C, 70.0 ; H, 5.2 per cent). If the period of heating be shortened (2-3 mins.), a mixtute of this cyano compound and the *acetyl* derivative of the oxime of (VIII, R=CHO) is obtained which may be separated by fractional crystallisation from alcohol. The latter, which is more soluble, separates in colorless prisms, m. p. 118°. (Found : N, 3.6. $C_{21}H_{21}O_6N$ requires N, 3.7 per cent). The compound is easily hydrolysed by acids to the aldehyde (VIII, R=CHO) and may be converted into the nitrile (VIII, R=CN) on further treatment with acetic anhydride.

Alternative Preparation of 6-*Methoxy*-3-(3 : 4-*dimethoxybenzyl*)-2-*acetocoumarone*.—A solution of the above nitrile (0.25 g.) in dry benzene (2 c. c.) was added dropwise in the cold to an excess of methylmagnesium iodide from methyl iodide (0.9 g.) and magnesium (0. 1 g.) in ether (15 c. c.). The mixture was refluxed for 1½ hours and left overnight. Next day, the mixture was carefully decomposed with ice-cold hydrochloric acid and the aqueous layer was quickly withdrawn. This deposited the ketone (VIII, R=COMe) on warming. The product was obtained from alcohol in cream-colored needles (0.22 g.), m. p. and mixed m. p. 156-57°.

6-*Methoxy*-3-(3 : 4-*dimethoxybenzyl*)-2-*propionylcoumarone* (VIII, R = COEt) was similarly prepared from ethylmagnesium bromide (ethyl bromide, 1.7g., magnesium, 0.3 g. and ether, 20 c. c.) and the foregoing nitrile (VIII, R = CN (0.4 g.). as a greenish product, which crystallised from a large volume of alcohol in cream-colored needles, m. p. 171°. (Found : C, 71.0 ; H, 6.2. $C_{21}H_{22}O_5$ requires C, 71.2 ; 6.2 per cent). The red solution of the compound in sulphuric acid turns on standing green and finally blue.

6-*Methoxy*-3-(3 : 4-*dimethoxybenzyl*)-2-n-*butyrylcoumarone* (VIII, R = COPr) was also similarly prepared from *n*-propylmagnesium bromide (propyl bromide, 2.0 g., magnesium, 0.3 g. and ether, 25 c. c.) and was crystallised from acetone-alcohol in cream-colored needles, m. p. 148°. (Found : C, 71.6 ; H 6.8. $C_{22}H_{24}O_5$ requires C, 71.8 ; H, 6.5 per cent). The compound dissolves in sulphuric acid with a red coloration which gradually turns green and finally blue.

The 2 : 4-*dinitrophenylhydrazone* crystallised from nitrobenzene-alcohol in deep red plates, m. p. 160-62°. (Found : N, 9.8. $C_{28}H_{28}O_8N_4$ requires N, 10.2 per cent).

6-*Methoxy*-3-(3 : 4-*dimethoxybenzyl*)-2-iso*butyryl oumarone* was exactly prepared as its isomer, mentioned above, by employing *iso*propylmagnesium bromide. The compound crystallised from acetic acid in nearly colorless needles, m. p. 124-25°. (Found : C, 71.5 ; H 6.9. $C_{22}H_{24}O_5$ requires C, 71.8 ; H, 6.5 per cent).

The *oxime* crystallised from aqueous methanol (80%) in colorless needles, m. p. 99-101°. (Found : N, 3.6. $C_{22}H_{25}O_5N$ requires N, 3.7 per cent). The red solution of the substance in sulphuric acid turns slowly green and finally blue.

Cyclisation of (VIII, R = COMe) : *Formation of* 3 : 8 : 9-*Trimethoxy*-6-*methyl*-β-*brazan.*—The ketone (VIII, R = COMe) (0.15 g.) was heated with glacial phosphoric acid (5 c. c.) in a boiling water-bath for 1 hour. The mixture turned slightly violet and gradually a microcrystalline solid appeared. After heating for 1/2 hour more, the product was worked up as usual. 3 : 8 : 9-Trimethoxy-6-methyl-β-brazan crystallised from pyridine in colorless, elongated hexagonal plates (0.8 g.), m. p. 241-42°. (Found : C, 74.3 ; H, 5.8. $C_{20}H_{18}O_4$ requires C, 74.5 ; H, 5.6 per cent). With sulphuric acid the compound develops a beautiful violet-red coloration which gradually turns purple and finally greenish blue.

Cyclisation of (VIII, R = COEt) : *Formation of* 3 : 8 : 9-*Trimethoxy*-6-*ethyl*-β-*brazan.*—A mixture of the ketone (0.3 g.) was heated and stirred carefully with glacial phosphoric acid (3 c. c.) at 180°-185°. The mixture at first became like a jelly and then a granular precipitate appeared. The product (IV, R = Et) crystallised from pyridine in colorless, shining needles, m. p. 188° (sintering at 184°) ; mixed m. p. with (VIII, R = COEt) was 155°. The analysis was, however not sharp. (Found : C, 73.9 ; H, 5.9. $C_{21}H_{20}O_4$ requires C, 75.0 ; H, 5.9 per cent). With sulphuric acid the compound develops a violet-red coloration which slowly turns purple and then green and finally blue.

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PRODUCTION OF THE JOSHI EFFECT IN OXYGEN UNDER SILENT ELECTRIC DISCHARGE. PART IX. INFLUENCE OF POWDERED WALL-MATERIAL

By S. R. Mohanty

Influence on the Joshi effect Δi, in 225 mm Hg. (31°) oxygen in a Siemens' tube, at various applied potentials V in the range 3 to 8 kV (r.m.s.) of 50 cycles frequency, of powdered wall-material (glass) has been studied. The discharge current i, the net *effect* Δi and the relative *effect* $\% \Delta i$, at constant V, are greater with gas only in the ionisation space ('normal' discharge) than with gas + powdered glass ('wall-influenced' discharge). The ratio i_{HF}/i_{LT} (of the high frequency H. F. to the total low tension L. T. current) in dark, at a fixed V, is greater for 'normal' than for 'wall-influenced' discharge, suggesting a diminution in the latter of the H. F. component of i. This has been confirmed by observations on the aerial current which is mainly H. F. The H. F. region of i constitutes the chief seat of the Δi phenomenon. Observed decrease of Δi therefore follows.

Oscillographic studies of the 'normal' discharge reveals that the current consists of a large number of distinct pulses per half-cycle. These pulses are absent below V_m, the 'threshold potential' and increase in number and height with $V > V_m$. Irradiation produces reduction in pulse heights, leading to Δi. In the 'wall-influenced' discharge, the height of the current pulses is greatly reduced; this reduction is the consequence of termination of electron avalanches on the powdered wall-material in the ionisation space. Further, the intensity of the external light received by the inner electrode and that half of the outer electrode farthest from the light source is low. Hence, the small Δi in 'wall-influenced' discharge, as observed.

The essentially surface origin of the Joshi effect Δi was inferred by Joshi (*Proc. Indian Sci. Cong.*, 1946, Part III, *Phys. Sec.*, Abst. No. 26; 1947, Abst. No. 25; *Curr. Sci.*, 1946, **15**, 281; 1947, **16**, 19) from the pronounced influence, on both the magnitude and sign of Δi, of the nature of the excited surface, and of 'ageing' under discharge. It appeared desirable therefore to study the variation of Δi, at constant applied potential V, with increase in the surface area of the (ozoniser) wall-material. This has now been done with a modified (glass) Siemens' tube in which the ionisation space could be filled with and emptied of powdered glass, the discharge being 'wall-influenced' and 'normal' respectively, in the total unfiltered L. T. current, and in the filtered H. F. and filtered L. F. The *effect* Δi has also been studied in the aerial current, and with a Du Mont cathode ray oscillograph.

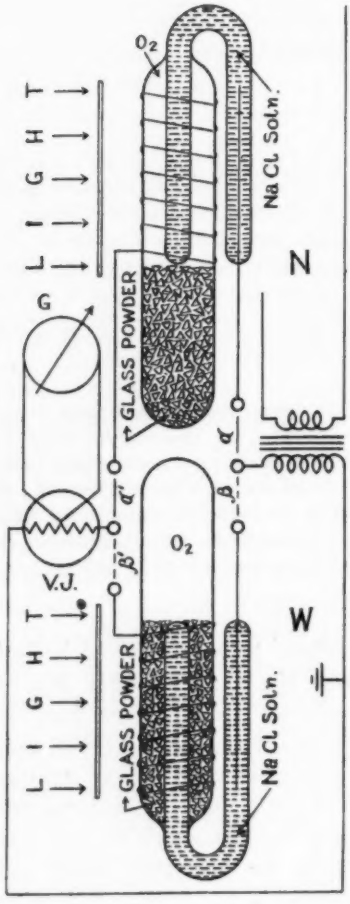
Experimental

The experimental arrangement and (a part of) the circuit are shown in Fig. 1. The discharge vessel, an all-glass Siemens' tube*, was filled with purified oxygen at an optimum pressure, in respect of Δi, of 225 mm. (31°) Hg. It also contained the

*Its dimensions are noted in the next page.

wall-material (glass) in coarsely divided form, and was so designed that it could be used, without disturbing the operative conditions, in two ways: When the powdered wall-material was outside the ionisation region; this is 'normal' discharge (N, Fig. 1). Then, by mere inversion of the discharge tube, the whole of the wall-material could be brought into the ionisation region; the discharge is now 'wall-influenced' (W, Fig. 1). The H. T. electrode consisted of a 10% solution of sodium chloride contained in the inner tube. A helix of bright copper wire, the distance between two consecutive turns being sufficiently large to permit irradiation of the enclosed gas, on the outer tube constituted the L. T. electrode. The tube was excited over 3 to 8 kV (r. m. s.) of 50 cycles frequency. The L. T. current was observed with a reflection galvanometer G actuated by Cambridge vacuo-junction (s) V. J. (Fig. 1). The source of light consisted of a battery of two 200 watt incandescent (glass) bulbs run at 200 volts, and placed at a distance of 17 cm. from the discharge tube. The *effect* Δi was observed (Table I) in the total (*i.e.* unfiltered) L. T. current, and in the filtered H. F. and L. F., the circuits (not shown in Fig. 1) being similar to those employed in Part VII (Mohanty, this *Journal*, 1950, **27**, 215). The value of the capacitance was 0.0004 μ_F, and that of the inductance, 250,000 μ_H. The mode of observation of Δi was similar to that described in Part I (Mohanty and Kamath, *ibid.*, 1948, **25**, 405). In Table II are recorded values, at different V, for i_{HF}/i_{LT} and i_{LF}/i_{LT}, in dark and under irradiation, for the 'normal' and the 'wall-influenced' discharges.

Fig. 1



* Dimensions of the Siemens' tube:

External diameter of the outer tube	...	19 mm.
Internal " " "	...	17
External " inner "	...	8
Internal " " "	...	6
Thickness of the glass wall	...	1
Inter-electrode distance	...	4.5
Length of the discharge space	...	22.0 cm.

TABLE I

Potential variation in the L. T. current of Joshi effect in oxygen produced 'normally' and under 'wall-influence'.

pO_2 = 225 mm. (31°). Temp. = 26°. 50~. Source of light = two 200 watt 200 volt incandescent (glass) bulbs, 17 cm. from the ozoniser.

V (kV, r. m. s.).		'Normal' discharge. (Gas only in the discharge space). Detector = vacuo-junction. Heater 9.11Ω 40Ω Dubilier across H terminals.			'Wall-influenced' discharge. (Gas + powdered wall-material in the discharge space). Detector = vacuo-junction. Heater 575 Ω.		
		L. T.	H. F.	L. F.	L. T.	H. F.	L. F.
3.74	i_D	...	...	...	...	...	...
	i_L	...	...	...	...	...	...
	Δi	...	...	...	...	...	...
	$\%\Delta i$	...	...	...	...	...	...
4.27	i_D	11.66	10.63	3.46	3.00	2.12	2.00
	i_L	7.35	7.14	2.45	3.00	2.12	2.00
	Δi	4.31	3.49	1.01	...	...	...
	$\%\Delta i$	37.0	32.8	29.2	...	...	...
4.81	i_D	14.15	13.04	4.12	3.87 (1.00)	2.83	2.83
	i_L	9.38	8.60	2.83	3.74	2.83	2.83
	Δi	4.77	4.44	1.29	0.13	...	...
	$\%\Delta i$	33.7	34.1	31.3	3.4	...	...
5.34	i_D	16.49	15.24	5.00	5.2	4.00	3.87
	i_L	11.32	10.63	3.61	5.1	3.94	3.81
	Δi	5.17	4.61	1.39	0.1	0.06	0.06
	$\%\Delta i$	31.4	30.3	27.8	1.9	1.5	1.6
5.87	i_D	18.44	17.35	5.66	6.08 (2.00)	4.47	4.69
	i_L	12.88	12.28	4.12	6.00	4.42	4.64
	Δi	5.56	5.07	1.54	0.08	0.05	0.05
	$\%\Delta i$	30.2	29.2	27.2	1.3	1.1	1.1
6.41	i_D	20.04	18.79	6.33	7.48	5.39	5.48
	i_L	14.29	13.64	4.58	7.38	5.34	5.43
	Δi	5.75	5.15	1.75	0.10	0.05	0.05
	$\%\Delta i$	28.7	27.4	27.7	1.3	0.9	0.9

TABLE I (*contd.*)

V (kV, r. m. s.)		'Normal' discharge. (Gas only in the discharge space). Detector = vacuo-junction. Heater 9. 11Ω, 40Ω Dubilier across H terminals.			'Wall-influenced' discharge. (Gas + powdered wall-material in the discharge space). Detector = vacuo-junction. Heater 575Ω.		
		L. T.	H. F.	L. F.	L. T.	H. F.	L. F.
6.94	i_D	21.23	19.97	6.56	8.83 (2.83)	6.33	6.40
	i_L	15.49	14.63	4.8	8.72	6.25	6.33
	Δi	5.74	5.34	1.76	0.11	0.08	0.07
	$\% \Delta i$	27.0	26.7	26.8	1.2	1.3	1.1
7.48	i_D	21.77	20.76	7.00	10.40	7.35	7.35
	i_L	16.15	15.69	5.2	10.30	7.28	7.28
	Δi	5.62	5.07	1.8	0.10	0.07	0.07
	$\% \Delta i$	25.8	24.4	25.7	1	1	1
8.01	i_D	22.27	21.23	7.14	11.79 (3.46)	8.49	8.31
	i_L	16.79	16.13	5.39	11.66	8.4	8.25
	Δi	5.48	5.10	1.75	0.13	0.09	0.06
	$\% \Delta i$	24.6	24.0	24.5	1.1	1.1	0.7

The bracketted figures in 'wall-influenced' are the i_D values obtained with the same vacuo-junction as used in 'normal'.

TABLE II

Proportion of the H. F. and the L. F. in the 'normal' and the 'wall-influenced' L. T. currents in dark and in light.

V (kV, r.m.s.)	'Normal' discharge. Dark		Light		'Wall-influenced' discharge. Dark		Light	
	$i_{HF}/i_{LT.}$	$i_{LF}/i_{LT.}$	$i_{HF}/i_{LT.}$	$i_{LF}/i_{LT.}$	$i_{HF}/i_{LT.}$	$i_{LF}/i_{LT.}$	$i_{HF}/i_{LT.}$	i_{LF}/i_{LT}
3.74	—	—	—	—	—	—	—	—
4.27	0.91	0.30	0.97	0.33	0.71	0.67	0.71	0.67
4.81	0.92	0.29	0.92	0.30	0.73	0.73	0.76	0.76
5.34	0.92	0.30	0.94	0.32	0.77	0.74	0.77	0.75
5.87	0.94	0.31	0.95	0.32	0.74	0.77	0.74	0.77
6.41	0.94	0.32	0.95	0.32	0.72	0.73	0.72	0.74
6.94	0.94	0.31	0.94	0.31	0.72	0.72	0.72	0.73
7.48	0.95	0.32	0.97	0.32	0.71	0.71	0.71	071
8.01	0.95	0.32	0.96	0.32	0.72	0.70	0.72	0.71

The Joshi effect was also observed in the aerial current. For this purpose, the L. T. electrode of the ozoniser was directly earthed. A moderately sized frame aerial was placed at a distance of 25 cm. from the ozoniser and was earthed through a vacuo-junction. When the ozoniser was excited at $V > V_m$ the 'threshold potential', it functioned as a source of H. F. radiations which were picked up by the aerial. Results for Δi in the aerial current i_{aerial} are shown in Table III.

TABLE III

Potential variation of the Joshi effect in oxygen in the aerial current.

p_{O_2} = 225 mm. (31°). Temp. = 26°. 50~. Detector = vacuo-junction. Source of light = two 200 watt 200 volt incandescent (glass) bulbs, 17 cm. from the ozoniser.

V (kV, r.m.s.).	'Normal' discharge				Wall-influenced' discharge	
	$i_{D.}$	$i_{L.}$	$\Delta i.$	$\%\Delta i.$	$i_{D.}$	$i_{L.}$
4.27	8.00	5.00	3.00	37.5	...	
4.81	10.00	6.56	3.44	34.4	1.41	
5.34	11.40	7.81	3.59	31.5	...	
5.87	12.51	8.86	3.65	29.2	1.73	
6.41	13.46	9.64	3.82	28.4	...	
6.94	14.39	10.39	4.00	27.8	1.73	
7.48	15.13	11.09	4.04	26.7	...	
8.01	15.97	11.79	4.18	26.2	2.00	

Oscillographic studies of the 'normal' and 'wall-influenced' discharges were made at various V with a Du Mont instrument. Input to this last was obtained from across 15 kΩ in the L. T. of the ozoniser. Fig. 3 contains a typical set of oscillograms for the two modes of discharge, in dark and under light.

DISCUSSION

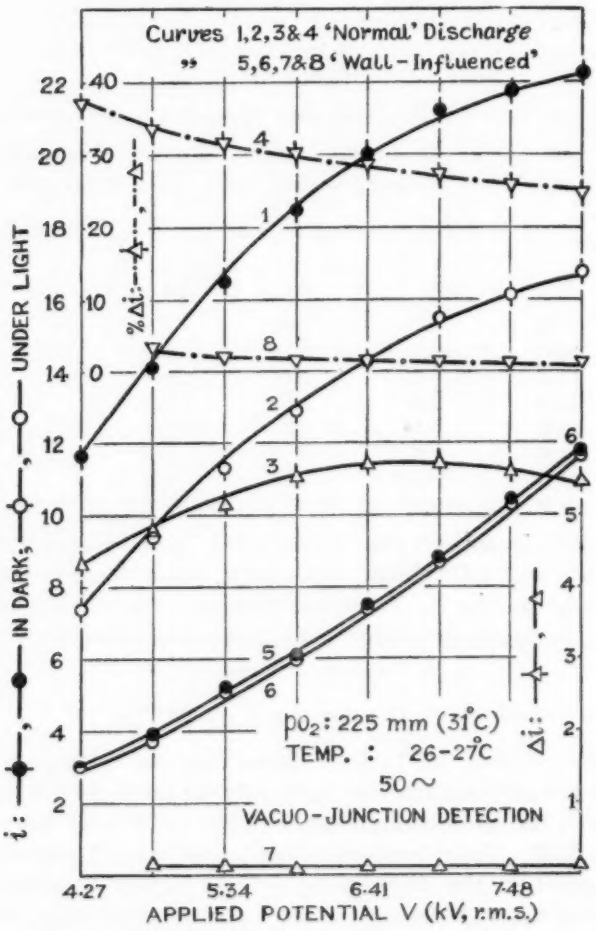
Examination of data in Table I shows that the system is non-conductive at 3.74 kV. Under 'normal' excitation, *i.e.*, with only the gas in the discharge space, values for the total L. T. current in dark at 4.81, 5.87, 6.94 and 8.01 kV are respectively 14.15, 18.44, 21.23 and 22.27. Under 'wall-influenced' excitation, *i.e.*, with the gas + powdered wall-material (glass) in the discharge space, the current at constant V is markedly diminished. Thus *e.g.*, with the same vacuo-junction as used under 'normal', values for dark i_{LT} at the above values of V, shown in parentheses in Table I, are as low as 1.00, 2.00, 2.83 and 3.46 respectively. This necessitated the use of a more sensitive vacuo-junction for studies of Δi under 'wall-influenced' excitation (cf. Table I).

The $V - i_{LT}$ characteristics, in dark and under light, for the 'normal' discharge (Fig. 2) are concave to the V-axis, indicating that the rise in i_{LT} with V, which is rapid near V_m, slows down at higher V. The same behaviour is exhibited by the corresponding characteristic curves for the filtered H. F. and the filtered L. F. Under 'wall-influenced' excitation, on the other hand, $V - i$ curves for the total (unfiltered)

L. T. (Fig. 2), the H. F. and the L. F., in dark and under irradiation, are convex to the V–axis, *i.e.*, the rise in i with V is more pronounced at higher than at low V.

Fig. 2

The Joshi effect in unfiltered L. T. in 'normal' and 'wall-influenced' discharges.



Whilst, similar to the observations of Mohanty and Kamath (*loc. cit.*), and Mohanty (*loc. cit.*; this *Journal*, 194[illegible] 26 553), both the net *effect* Δi and the relative *effect* $\%\Delta i$ for the 'normal' discharge vary markedly with V (Fig. 2; cf. Table I) under 'wall-influenced' excitation, the variation of Δi, in the unfiltered L. T. as well as in the filtered H. F. and the filtered L. F., with V is not marked. Further, the lowest V at which Δi occurs in this case is higher than the corresponding potential under 'normal' excitation. Thus, Δi makes its appearance at 4.27 kV under 'normal', whereas under 'wall-influenced' excitation and in the unfiltered L. T., at 4.81 kV,

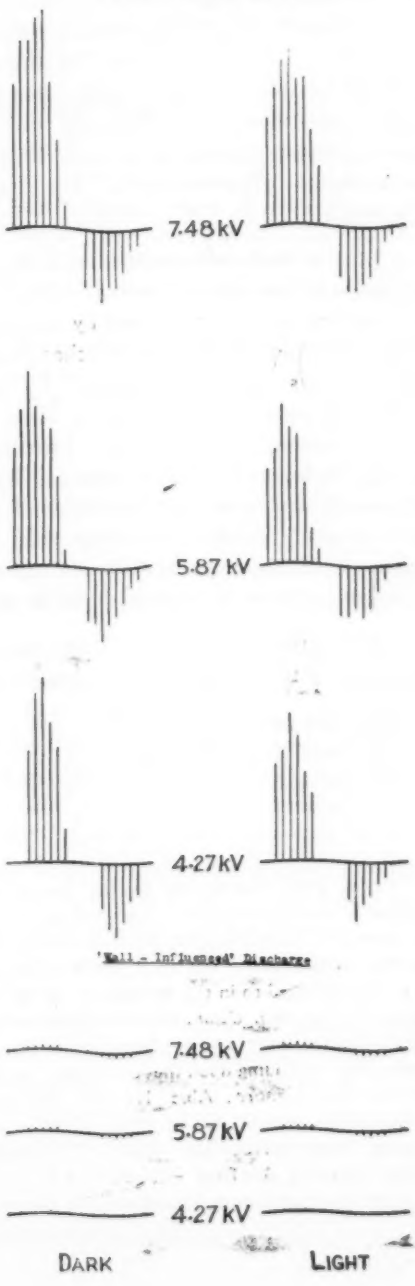
At constant V, both Δi and $\%\Delta i$ are markedly smaller under 'wall-influenced' than under 'normal' excitation. Thus, under the former, at 5.87 kV, Δi in the unfiltered L T. is as low as 0.08, whereas under the latter at the same V, 5.56. The corresponding values of $\%\Delta i$ are respectively 1.3 and 30.2. In the filtered H. F. and the filtered L F., at the above V, values for $\%\Delta i$ are respectively 29.2 and 27.2 under 'normal', and 1.1 and 1.1 under 'wall-influenced' excitation.

It will be evident from data in Table II that under 'wall-influenced' excitation, the proportion of the H. F. in the L. T. current is smaller, at constant V, than under 'normal' excitation. Thus *e. g.*, whereas the ratio i_{HF}/i_{LT} in dark is, at 4.27 kV, 0.91 under 'normal', it is, at the same V, 0.71 under 'wall-influenced' discharge. That it is the high frequencies which suffer reduction in the latter will also be evident from an examination of the magnitude of the aerial current (Table III) which is chiefly H. F. Thus, at 5.87 kV, i_{aerial} in dark for the 'normal' discharge is 12.51 and as low as 1.73 for the 'wall-influenced' discharge. Since Δi occurs preferentially in the H. F. region of i (Joshi, *Nature*, 1944, **154**, 147; *Curr. Sci.*, 1945, **14**, 67; Mohanty, this *Journal*, 1950, **27**, 215), reduction of the proportion of the same in the total (unfiltered) L. T. which obtains under 'wall-influenced' excitation would reduce Δi, as observed.

Examination of the structure of the discharge current (Fig. 3) with the cathode ray oscillograph reveals, besides the frequency of the A. C. supply, a remarkably large

Fig 3

Oscillograms of the silent discharge, 'normal' and 'wall-influenced' at diff. applied potentials



number of higher frequencies of widely varying strengths (cf. Joshi, *Nature*, 1944, **154**, 147 ; *Curr. Sci.*, 1944, **13**, 253 ; *Proc. Ind. Acad. Sci.*, 1945, **A22**, 389 ; Deb and Ghosh, *Sci. & Cult.*, 1946-47, **12**, 17 ; 1948, **14**, 39 ; this *Journal*, 1948, **25**, 449 ; Harries and Engel, *J. Chem. Phys.*, 1951, **19**, 514). These high frequency pulses are absent at $V<V_m$, and increase in number and amplitude with V increased beyond V_m. *Ceteris paribus*, reduction of the pulse heights leads to Δi* ; this reduction is proportionately less at higher than at low V. This is for the 'normal' discharge. Under 'wall-influenced' discharge, on the other hand, the high frequency pulses are almost completely suppressed, and no further diminution in amplitude is perceptible on irradiation. The magnitude of Δi in the 'wall-influenced' discharge is therefore very small.

In the 'wall-influenced' discharge, the number of gas molecules in the applied field is much less than in 'normal', since in the former case most of the volume of the discharge space is occupied by powdered glass. The number of primary electrons is less. Further, electron avalanches starting from the electrodes, and those created within the gas mass, get arrested by the powdered wall-material. The height of the current pulses is consequently less, and Δi smaller, in 'wall-influenced' than in 'normal' discharge, as observed. Moreover, whilst in the 'normal' discharge both the electrodes receive the external light at almost the same intensity, in the 'wall-influenced' discharge the central and the farthest half of the outer electrode get light of much reduced intensity than that half of the outer electrode nearest the lamps. In consequence, the already attenuated current pulses in the 'wall-influenced' discharge suffer no further appreciable suppression on irradiation.

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* The total current i_{LT} flowing through a discharge vessel at a given V ($>V_m$) consists of frequencies ranging from the supply to those in the radio regions, together with a small D. C. due to rectification. The indicator shows the (vector) resultant of the i values due to the various frequencies prevailing at the instant. The H. F. which constitutes a major part of i_{LT} is the chief seat of the negative *effect* $-\Delta i$ (referred to in the text simply as Δi, since it is apparently more familiar), and very high (Shukla, *J. Phys. Coll. Chem.*, 1949, **53**, 1239) and medium (B. B. Prasad, *Proc. Ind. Acad. Sci.*, 1949, **29 A**, 322) frequencies of the *positive effect* $+\Delta i$, an increase in i_D on irradiation. Oscillographic studies have revealed that depending upon the conditions, $+\Delta i$ and $-\Delta i$ co-occur (Joshi, *Proc. Indian Sci. Cong.*, 1947, Part III, *Phys. Sec.*, Abst. No. 25). The former is characterised by an increase, under irradiation, in the number or/and the amplitude of the pulses, and the latter by an opposite change ; the current indicator shows the balance. Amplitude increase of some of the pulses in the 'normal' discharge is evident from Fig. 3. That $-\Delta i$ in i_{HF} is not appreciably larger than that in i_{LT} (Table I) can be traced to the simultaneous occurrence of $+\Delta i$.

[Jour. Indian Chem. Soc., Vol. 30, No 1, 1953]

RESONATING SEMIPOLAR SINGLE BOND. PART VIII. HYPERCONJUGATION, STRENGTH OF ACIDS AND CALCULATION OF DIPOLE MOMENTS

By Saiyid Shamim-Ahmad and M. A. Wajid

An alternative mechanism of hyperconjugation is put forward on the basis of the theory of the resonating semipolar single bond which is similar to Baker and Nathan's assumption and different from wave mechanical ideas as advanced by Pauling, Wheland and Mulliken. Wave mechanical representation is criticised on the grounds : (*i*) it assumes free ions as contributing structures, (*ii*) neglects the nature of the links, and also (*iii*) neglects the nature of the activating group. Active methylene compounds are shown to constitute a serious objection to the correctness of the theory as applied to hyperconjugation.

The mechanism on the basis of the theory of the resonating semipolar single bond is used to explain the shortening of bond lengths, strength of acids and the calculation of dipole moments of halogenated methanes. Calculated results thus obtained are very close to the observed values, whereas earlier calculations gave far divergent results.

Baker and Nathan (*J. Chem. Soc.*, 1935, 1844) put forward the concept of hyperconjugation to explain the abnormal behaviour of certain series of alkyl substituted compounds. They suggest that the duplet of electrons forming the C−H bond of an alkyl group, which is attached to an unsaturated carbon atom, is less localised than that in a similar C—C bond ; hence, electron release is permitted by a mechanism which is essentially a type of tautomeric effect : $H-\overset{|}{\underset{\downarrow}{CH_2}}-\overset{\curvearrowright}{C}-C$. Pauling and others (*J. Amer. Chem. Soc.*, 1939, **61**, 927 ; Wheland, *J. Chem. Phys.*, 1934, **2**,474) treat it as due to resonance in which ions and radicals behave as contributory structures, while in another treatment (Mulliken, Ricki and Brown, *J. Amer. Chem. Soc.*, 1941, **63**, 41) it is supposed to result from the conjugation of unsaturated centres with 'quasi multiple' bonds composed of a number of single bends :—$H_3\equiv\overset{\curvearrowright}{C}-C-\overset{\curvearrowright}{C}-$

There are a number of difficulties with the wave mechanical concepts. Absence of colour indicates that resonance should not be postulated in an extreme form ; even by itself contribution by ions and radicals appears to be improbable. A further difficulty is that these concepts do not take into consideration the nature of the links. Thus H−C links should behave in the same way as C−C links This is obviously against facts. Nor do they consider the nature of the activating group, whereas in point of fact, hyperconjugation is markedly dependent upon the attached group. Moreover, cases of hyperconjugation involving only single bonds are also known. Thus, methylchloroform and chloroform have a value of μ equal to 1.8 and 1.15 respectively. This is interpreted as a second order hyperconjugation (Hurdis and Smyth, *ibid.*, 1942, **64**, 2829), but the influence observed is much too large to be a second order effect and casts serious doubt on wave mechanical interpretations so far advanced. The inadequacy of these interpretations is clearly

indicated by compounds containing active hydrogen. The hyperconjugational resonance possibilities are in the order : $CH_3 > CH_2 > CH$ and this also should be the order of ionisability. Actually just the reverse is the case. Another point to be noted is that the activating groups may be the same or different, but the influence will be the same. This clearly points to the conclusion that hyperconjugation is nothing more than the possibility of conjugation of single bonds with other groups under the strong polarising influence of those groups. The theory of the resonating semipolar single bond puts forward the mechanism for such a type of conjugation. Baker and Nathan (*loc. cit.*) have cautiously remarked that the duplet in C–H is less localised than C–C bonds. It may be said that the polarising influences can semipolarise single bonds depending upon the polarising intensity of the group. Thus, a hyperconjugated system may be represented in an extreme forms as —

$$H-CH_2-C=C \longrightarrow H^{+\frac{1}{2}} \cdots CH_2 \cdots C^{-\frac{1}{2}}$$

C. Actually mesomeric part of the semipolarisation of single bonds comes into play. We can on this basis easily determine the groups which will lead to semipolarisation of single bond by considering the properties of the compound HX. If HX can behave as an acid, the group X may be supposed to be capable of semipolarising the single bond between itself and hydrogen. Thus, the following groups may be supposed to be capable of semipolarising single bonds : –Cl, –Br, –I, –SH, –C≡C, –COOEt, –CN, $-NO_2$ etc. Weaker influences are : C=C, –OH, >CO etc.

Bond Lengths

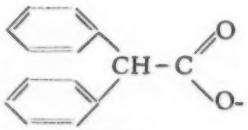
C≡C, C≡N show their semipolarising influence in reducing the C–C bond length by 0.08 Å in methylacetylene, dimethylacetylene, dimethyldiacetylene, diacetylene, cyanogen and methyl cyanide (Pauling and others, *loc. cit.*). We may represent the molecules with a semipolar single bond as an extreme form :

$$H-CH_2-C\equiv C \longrightarrow H^{+\frac{1}{2}} \cdots CH_2 \cdots C^{-\frac{1}{2}}$$

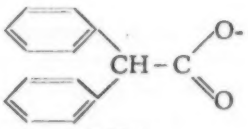
Besides, a number of other structures may be written for the molecules. The presence of these resonating structures would stabilise hydrogen, and hence the acidic nature will not be so marked as in acetylene. Semipolarisation of hydrogen bonds results in the double bond character of C–C bond, and hence the shortening observed. The weak polarising influence of C=C influences adjacent single bonds but little (Pauling and Brockway, *J. Amer. Chem. Soc.*, 1937, **59**, 1223). In chlorine compounds the inductive effect is prominent at the expense of the semipolarising tendency. Still it will be present to a certain extent which should lead to the development of this effect. The hyperconjugation can be shown better by iodine compounds where inductive effect being small due to equal electronegativity of the two atoms, semipolarisation is much more important. Still the shortening of the bond should take place in methylchloroform where the increase in dipole moment over chloroform has been suggested to be due to hyperconjugation (Hurdis and Smyth, *loc. cit.*).

Strength of Acids

Though a large amount of work has been done on the dissociation constant of acids, and a large number of electronic influences postulated, still the problem is not fully settled yet. Jenkins (*J. Chem. Soc.*, 1940, 1448) has added one more postulate. He starts with the work of Sidwick (*ibid.*, 1937, 694) and of Lennard-Jones and Coulson (*Trans. Faraday Soc.*, 1939, 35, 822) which show that there is a linear relationship between resonance energy and '*n*', where '*n*' is the number of canonical forms for the molecules. He strives to show that extremely simple relations exist between '*n*' or some function of '*n*' and dissociation constant and activation energies. To get the requisite number of canonical forms in the case of phenyl- and diphenylacetic acids he assumes the following structures of some canonical forms :—

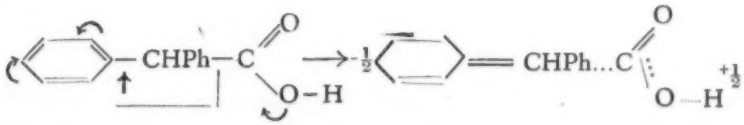


[I]

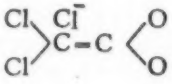


[II]

He admits that no simple picture of the interaction can be given. It appears that two resonating structures at the end of a molecule can lead to a further stabilisation without the molecule resonating as a whole. If it were so, the length of the bond will be without any influence. To account for the value of '*n*' required, the resonance forms may be introduced by employing the postulate of the resonating semipolar single bond :

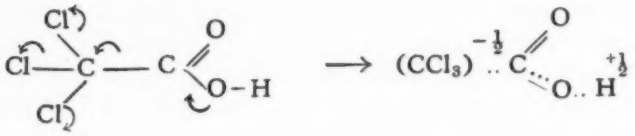


Similarly to account for the strength of trichloroacetic acid he supposes the forms to be :



This representation will lead to the impresssion that C–C bond is very strong in trichloroacetic acid. In fact, carbon bonds are greatly weakened by the presence of chlorine substituents, e.g. CCl_3CHO is easily converted into $CHCl_3$, and CI_3CHO is still more readily converted into CHI_3. These difficulties may be removed easily if we represent the electron transfer in this case also by the semipolarisation of single bonds. Inductive effect is not sufficient by itself to account for the strength

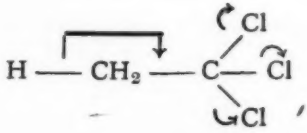
of trichloroacetic acid, as on that basis it should be as strong as monochloroacetic acid. Semipolarisation of single bonds in this case can be represented as :



This representation will indicate both the strength of the acid and the weakness of the C–C bond.

Dipole Moments

The large increase in dipole moment of methylchloroform as compared with chloroform was attributed by Maryott, Hobbs and Gross (*J. Amer. Chem. Soc.*, 1941, **63**, 659) to a transfer of charge from the methyl carbon atom to the adjacent carbon atom and the transfer in turn of some of this charge to the chlorine atom. This is essentially a hyperconjugation of the second order, which is assumed by wave mechanical representation to be present in CH_3-CH_3. It was first discussed from this point of view by Hurdis and Smyth (*loc. cit.*). It is clear that hyperconjugation of the second order should not be so very inportant as is actually the case with this compound. On the present theory we can explain it as



In fact, the present ideas can be used to calculate the dipole moments of halogenated alkanes. CH_4 is non-polar and so it is obvious that H and CH_3 are balancing each other. This being so, the difference between the dipole moments of HCl ($\mu=1.03$) and CH_3Cl ($\mu=1.86$) cannot be easily understood unless we make the assumption that the presence of chlorine is influencing C–H bonds. The nature of this influence cannot be pictured on any other ground except that of the theory of the resonating semipolar single bond. Due to polarisation HCl has a dipole moment of 1.03. If no other factor interfered, CH_3Cl would also have a dipole moment of about the same value. But the polarising nature of chlorine enables carbon to polarise attached C–H bonds to a certain extent. As actual semipolarisation has not taken place (absence of colour etc.) only the mesomeric part will be available. As semipolarisation means the total removal of electrons from molecular to the atomic orbital of one of the atoms, it will be treated as a scalar quantity. On this basis $\mu CH_3Cl-\mu HCl$ or $0.83D$ is the scalar sum of the semipolarisation brouhgt about under the influence of Cl. The contribution of each of the hydrogen

atoms may therefore be placed at 0.83/3 or 0.28. As chlorine can accommodate one full electron, this amount of semipolarisation may be taken as the maximum mesomeric influence under the joint inductive and semipolarising effect of chlorine. If the inductive effect is less, as in Br and I compounds, the contribution due to semipolarisation will be greater, e. g. $\mu CH_3Br - \mu HBr = 1.80 - 0.78 = 1.02\,D$, $\mu CH_3I - \mu HI = 1.66 - 0.38 = 1.28\,D$. Calculating on this basis and adding the moments vectorially we have the following table indicating the actual dipole moments of the halogenated methanes and the values calculated on the basis of present ideas and the values calculated on the basis of mere vector addition with $1.86\,D$ as the values C–Cl dipole. It will be noticed that the results aggree closely with the observed values (Table I).

TABLE I

Dipole moment of halogenated methanes.

Compounds.	Calculated.	Actual.	Calculated (older).
CH_3Cl	...	1.86	...
CH_2Cl_2	1.58	1.58	2.14
$CHCl_3$	1.12	1.15	1.86
CH_3Br	...	1.80	...
CH_2Br_2	1.35	1.39	2.07
$CHBr_3$	0.90	0.99	1.80
CH_3I	...	1.66	...
CH_2I_2	1.01	1.10	1.91
CHI_3	0.52	0.91	1.66

The only divergent value is in the case of iodoform. This is an exception that proves the rule as only iodoform of the above compounds is deeply coloured. This indicates that actual resonance has started. A similar phenomenon is met with in the case of *p*-nitroaniline where the increase in the dipole moment above the sum of the substituents is accompanied by the appearance of a deep colour.

Some other results for other types of chlorine derivatives of hydrocarbons are given in the table below. The results have been calculated by assuming that the hyperconjugational effect, the conferring as it does some double character, must be compounded vectorially in compounds such as

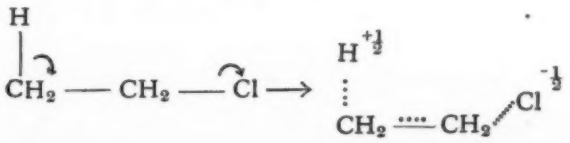


TABLE II

Substance.	Calc.	Obs.	Substance.	Calc.	Obs.
C_2H_5Cl	2.02	2.06	$CH_2 : CHCH_2Cl$	2.02	2.01
CH_3CHCl_2	2.03	2.07	*cis*-CHCl : CHCl	2.02	1.89
CH_3CCl_3 (app.)	1.86	1.79	C_6H_5Cl	...	1.52
$CH_3CH_2CH_2Cl$	2.02	2.04	*o*-$C_6H_4Cl_2$	2.13	2.25
$(CH_3)_2CHCl$	2.20	2.18	*m*-$C_6H_4Cl_2$	1.46	1.48
$CH_3CH : CHCl$	1.67	1.66	*p*-$C_6H_4Cl_2$	0.00	0.00

The authors' sincerest thanks are due to Dr. S. S. Joshi of the Hindu University for his keen interest in the work. One of us has also to thank Prof. S. K. K. Jatkar for his interest in the work, sympathetic criticism and spontaneous hospitality.

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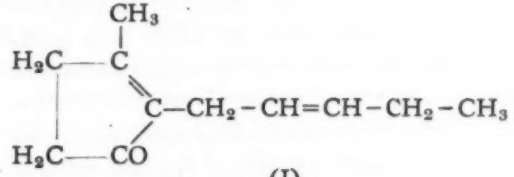
SYNTHESIS OF FIVE AND SIX MEMBERED RING KETONES WITH A LONG SIDE-CHAIN FOR USE AS PERFUMES

By S. M. Gupta and S. S. Deshapande

Synthesis of 2-*n* heptyl*cyclo*pentanone, 2-*n*-heptyl*cyclo*hexanone, 3-methyl-5-*n*-heptyl*cyclo*pentanone, 2-geranyl*cyclo*hexanone by attachment of the long side-chain to the corresponding five or six membered ring ketone is described. Preparation of 2-hexyl-3-methyl-Δ^2-*cyclo*pentenone by Frank's method is also described. When the side-chain is in position-2 the synthetic product can act as a perfume.

Jasmone (I), the odoriferous principle of jasmine blossom, was first isolated by Hesse (*Ber.*, 1899, **32**, 2617). The assignment of its structural formula involving a five-membered ring was done independently by Treff and Werner (*Ber.*, 1933, **66**, 1521) and by Ruzicka and Pfeiffer (*Helv. Chim. Acta*, 1933, **16**, 1208). Its presence in the extract of neroli and jonquil flowers was claimed by Elze (*Reichstoffindustrie*, 1926, **19**, 181).



(I)

Its synthesis was achieved by Treff and Werner (*Ber.*, 1935, **68**, 640) and also independently by Hunsdiecker (*Ber.*, 1942, **75**, 442).

The synthesis of other five or six-membered ring ketones having a long side-chain in position-2, with or without a double bond at Δ^2 and with or without a methyl group in position 3, was achieved by a number of workers (Treff and Werner, *loc. cit.*), Plattner and Pfau (*Helv. Chim. Acta*, 1937, **20** 1474), Hudsdiecker (*loc. cit.*), Staudinger and Ruzicka (*Helv. Chim. Acta*, 1924, **7**, 245) and it was found that generally these products could act as synthetic perfumes (Werner, *Fette U. Seifen*, 1938, **45** 623).

In general, these methods consist in first preparing an open-chain molecule with one or more carbonyl groups and a long carbon chain in the desired position and then cyclising the same. The ketones described in this paper have been synthesised by us differently. *cyclo*Pentanone, *cyclo*hexanone and 3-methyl*cyclo*-pentanones were treated with sodamide in benzene and by reacting the sodium compound, so formed, with terminally halogen-substituted carbon chain, the latter was attached to the ring obviously in α-position. The chain contained from six to ten carbon atoms. 2-*n*-Heptyl*cyclo*pentanone (II), 2-*n*-heptyl*cyclo*hexanone (III), 3-methyl-*5-*n*-heptyl*cyclo*pentanone (IV) and 2-geranyl*cyclo*hexanone (V) have thus been prepared.

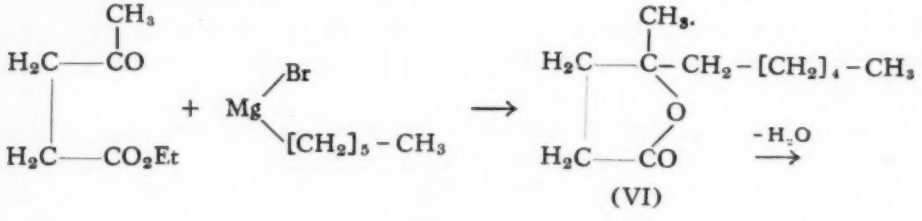
* Position-5 by inference.

These ketones with the exception of (IV) yield semicarbazones whose analysis agrees with their expected composition.

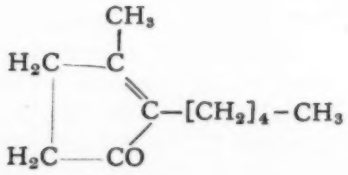
By catalytic reduction of 2-*n*-heptyl-Δ^2-*cyclo*pentenone Plattner and Pfau (*loc. cit.*) obtained the corresponding *cyclo*pentanone which should be (II). As however, they observed the boiling point of the ketone at a different pressure than ours, and have not described the semicarbazone, a comparison of their ketone with ours could not be made. We have failed to obtain a benzylidene derivative of the ketone under conditions described by them. (III) was prepared by Heine & Co. (A. G. Fr., 46, 956, Nov. 23, 1939) by catalytic reduction of the corresponding Δ^2-*cyclo*hexenone. No derivative has been described by them. Both (II) and (III) have an agreeable odour, that of (III) being more intense.

The *n*-heptyl-3-methyl*cyclo*pentanone, now prepared, seems from analytical data to be a pure compound. It has, however, not yielded any derivative. Since the methyl group in position-3 causes steric hindrance in position-2 (cf. Ruhemann, *J. Chem. Soc.*, 1912, **101**, 1736.; also Agarwal and Deshapande, this *Journal*, 1951, **28**, 65), the heptyl group appears to enter in position-5 and the structure is probably of (IV). The isomeric 2 heptyl-ketone is described by Heine & Co. (A. G. Ger., 613,308, May 16, 1935) as a synthetic perfume. Our ketone is absolutely without any odour. 2-Geranyl*cyclo*hexanone (V) does not seem to have been described in literature. It has an odour resembling ginger.

Dihydrojasmone (VII) (3-methyl-2-*n*-amyl*cyclo*pentenone) was prepared by Frank (*J. Amer. Chem. Soc.*, 1944, **66**, 4) by treating magnesium-*n*-hexyl bromide with levulinic ester which gave the lactone (VI). The latter on distillation over phosphorus pentoxide in vacuum yielded the ketone. We have prepared its higher homologue, 3-methyl-2-*n*-hexyl*cyclo*pentenone (VIII) by Frank's process using *n*-heptyl bromide. The identity of (VIII) with that prepared by Hunsdiecker (*loc. cit.*) by a different process was proved by comparison of the melting points of the semicarbazones and by analysis of the same.



(VI)



(VII)

EXPERIMENTAL.

2-n-*Heptyl*cyclo*pentanone* (II).—Sodamide (5.8 g., coarse granule, B. D. H.) was added in instalment to *cyclo*pentanone (12.6 g.) in dry benzene (50 c. c.). The mixture was refluxed on a water-bath under dry conditions till ammonia ceased to be evolved (7 hours). *n*-Heptyl bromide (27.0 g., 178°-180°) was then added and the heating continued until the mixture showed slight alkalinity (10 hours). More heptyl bromide (about 2 g.) was added and the heating continued until the mixture was neutral. The product was then poured into water, the benzene layer separated, washed, dried over calcium chloride and the solvent distilled off. On fractionating the residue, a pale yellow liquid distilled at 158°-159°/16 mm. (130°/10 mm. A. S. Pfau, U. S. P. 2069/861, 1937), yield 6.2 g. It has a faint but a pleasant odour. (Found : C, 78.5 ; H, 11.7. Calc. for $C_{12}H_{22}O$: C, 79.1 ; H, 12.1 per cent).

Its semicarbazone crystallised from alcohol, m. p. 160°. (Found : N, 17.9. $C_{13}H_{25}O\,N_3$ requires N, 17.5 per cent).

2-n-*Heptyl*cyclo*hexanone* (III) was prepared in the manner as above using sodamide (3.9 g.), *cyclo*hexanone (9.8 g.) and *n*-heptyl bromide (18.0 g.). It is a pale yellow liquid with a pleasant odour and it boils at 176°-178°/18 mm., yield 5.0 g. (Found : C, 79.3 ; H, 12.5. Calc. for $C_{13}H_{24}O$: C, 79.6 ; H, 12. 2 per cent).

Its semicarbazone crystallised from alcohol, m. p. 183°. (Found : N, 17.1. Calc. for $C_{14}H_{27}O\,N_3$: N, 16.6 per cent).

3-*Methyl*-5-n-*heptyl*cyclo*pentanone* (IV) was prepared in a similar way as above from sodamide (3.9 g.), 3-methyl*cyclo*pentanone (9.8 g.) and *n*-heptyl bromide (18.0 g.), yield 4.5 g., b. p. 168°-170°/18 mm. (Found : C, 79.1 ; H, 11.6. Calc. for $C_{13}H_{24}O$: C, 79.6 ; H, 12.2 per cent).

2-*Geranyl*cyclo*hexanone* (V) was prepared from sodamide (15.6 g.), *cyclo*hexanone (14.1 g.) and geranyl chloride (b. p. 104°-105°/10 mm., 24.8 g.). It is a pale yellow liquid with ginger like odour and distils at 164°-166°/10 mm., yield 7.1 g. (Found : C, 81.6 ; H, 11.5. $C_{16}H_{26}O$ requires C, 82.1 ; H, 11.1 per cent).

Its semicarbazone crystallises from alcohol and melts at 187°. (Found : N, 14.7. $C_{17}H_{29}ON_3$ requires N, 14.4 per cent).

2-*Hexyl*-3-*methyl*-Δ^{1}-cyclo*pentenone* (VIII) : *Formation of Lactone.*—Grignard reagent prepared from magnesium (2.4 g.) and *n*-heptyl bromide (17.9 g.) in dry ether was gradually added to ice cold ethereal solution of ethyl levulinate (15 g.). After standing at 0° for one hour and then at room temperature for another hour, the reaction mixture was poured into cold dilute sulphuric acid. After extraction with ether, washing, drying, and removal of the solvent, the lactone obtained distilled as a pale yellow, mobile liquid at 146°-148°/12 mm., yield 4.8 g.

It has a peach like odour. Considerable amount of a high boiling liquid was left after fractionation of the lactone. (Found : C, 71.9 ; H, 11.6. Calc. for $C_{12}H_{22}O_2$: C, 72.7 : H, 11.1 per cent).

On adding phosphorus pentoxide (2.5 g.) to the lactone (4.6 g.) in a small distilling flask and warming, the contents turned black. The mixture was distilled at a low pressure when 2.6 g. of a light yellow, mobile liquid with a strong pleasant odour, b. p. 126°-128°/12 mm., (Hunsidecker, *loc. cit.*, gives b. p. 144°/18 mm.) was obtained. As the amount of the ketone was too small for purification, the crude ketone was turned into its scmicarbazone. The latter, crystallised from alcohol, melts at 165° (Hunsdiecker, *loc. cit.* gives m. p. 164°). (Found : N, 18.3. Calc. for $C_{13}H_{23}O\,N_3$ requires N, 17.7 per cent).

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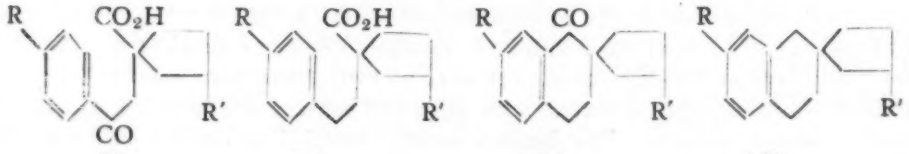
STUDIES IN CATALYTIC DEHYDROGENATION. PART II

By Suresh Chandra Sen Gupta and D. N. Chatterjee

1 : 2 : 3 : 4-Tetrahydronaphthalene-2 : 2-spiro-(3′-methyl*cyclo*pentane) and its 7-methyl derivative have been synthesised and their catalytic dehydrogenation with Pt-C studied. The former gave 2-methylphenanthrene as the only dehydrogenation product, whereas the latter gave 3 : 6-dimethylphenanthrene along with a small amount of anthracene derivatives.

We synthesised the two tetrahydronaphthalene-spiro-*cyclo*pentanes, namely 1 : 2 : 3 : 4-tetrahydronaphthalene-2 : 2-spiro-(3′-methyl*cyclo*pentane (IV, R−H ; R′−Me) and its 7-methyl derivative (IV, R−R′−Me), each having a methyl group in the spiro-*cyclo*pentane ring, in order to study the behaviour of the methyl group during catalytic dehydrogenation of these spiro-compounds. It was found that the spiro-hydrocarbon (IV, R−H ; R′−Me) underwent simultaneous dehydrogenation and ring transformation when heated with Pt-C catalyst at 300°-320° with the formation of 2-methylphenanthrene as the only product. The formation of any anthracene derivative could not be detected. When the spiro-hydrocarbon (IV, R−R′−Me), however, was dehydrogenated under a similar condition, it was, found that though the main dehydrogenation product was 3 : 6-dimethylphenanthrene, a small amount of a high melting hydrocarbon could be isolated which seemed to be a mixture of 2 : 6-dimethyl- and 2 : 7-dimethylanthracenes. So it was found that in both the cases though ring transformation took place during catalytic dehydrogenation, the methyl group present in the spiro-*cyclo*pentane ring was not expelled.



(I) (II) (III) (IV)

The two spiro-hydrocarbons were synthesised by an extension of the method followed in Part I of this series (this *Journal*, 1952, **29**, 331). The anhydride of 3-methyl*cyclo*pentane-1-carboxy-1-acetic acid was condensed with benzene in presence of aluminium chloride affording α-(3′-methyl*cyclo*pentane)-β-benzoylpropionic acid (I, R=H ; R′=Me) and this on Clemmensen reduction gave α-(3′-methyl*cyclo*pentane)-γ-phenylbutyric acid (II, R=H ; R′=Me) (Desai and Wali, *Proc. Ind. Acad. Sci.*, 1937, **6A**, 141). The latter on cyclisation with 85% sulphuric acid gave 1-keto-1 : 2 : 3 : 4-tetrahydronaphthalene -2 : 2-spiro-(3′-methyl*cyclo*pentane) (III, R=H ; R′=Me). The spiro-ketone on Clemmensen reduction gave 1 : 2 : 3 : 4-tetrahydronaphthalene-2 : 2-spiro-(3′-methyl*cyclo*pentane) (IV, R=H ; R′=Me).

In a similar manner 7-methyl-1 : 2 : 3 : 4-tetrahydronaphthalene-2 : 2-spiro-(3′-methyl*cyclo*pentane) (IV, R−R′−Me) was synthesised starting from toluene

and anhydride of 3-methyl*cyclo*pentane-1-carboxy-1-acetic acid. Structures of the keto-acids (I, R=H ; R′=Me) and (I, R=R′=Me) had been proved by Desai and Wali (*loc. cit.*) as containing a $CH_2.CO$ grouping.

EXPERIMENTAL

«-(3′-Methyl*cyclo*pentane)-β-benzoylpropionic acid (I, R=H ; R′=Me) and «-(3′-methyl*cyclo*pentane)-γ-phenylbutyric acid (II, R=H ; R′=Me) were prepared according to Desai and Wali (*loc. cit.*). This butyric acid was best purified by distillation under reduced pressure and crystallisation from petroleum ether.

1-*Keto*-1 : 2 : 3 : 4-*tetrahydronaphthalene*-2 : 2-*spiro*-(3′-*methyl*cyclo*pentane*) (III, R=H; R′=Me).—The butyric acid (II, R=H ; R′=Me) (7g.) was heated with 85% sulphuric acid (28 c.c.) at 100° for 1½ hours with stirring. The product was poured on ice, extracted with ether and the ether extract was washed with dilute ammonia, dried and distilled. It is a viscous oil with a characteristic odour, b. p. 137°–140°/5mm., yield 5 g. (Found : C, 83.9 ; H, 8.5. $C_{15}H_{18}O$ requires C, 84.1 ; H, 8.4 per cent).

1 : 2 : 3 : 4-*Tetrahydronaphthalene*-2 : 2-*spiro*-(3′-*methyl*cyclo*pentane*) (IV, R=H ; R′=Me).—The spiro-ketone (III, R=H ; R′=Me) (5 g.) was boiled with amalgamated zinc (20 g.) and concentrated hydrochloric acid (20 c. c.) for 24 hours. The product was a colorless liquid, b. p. 122°-125°/5 mm., yield 3 g. (Found : C, 89.7 ; H, 10.2. $C_{15}H_{20}$ requires C, 90.0 ; H, 10.0 per cent).

Dehydrogenation of the Spiro-hydrocarbon (IV, R=H ; R′=Me).—The spiro-hydrocarbon (3 g.) was heated with Pt-C catalyst (0.3g.) in a metal-bath at 300°-310° for 6 hours and at 310°-320° for 6 hours when no further hydrogen was evolved. The product was thoroughly extracted with ether and benzene and distilled over sodium under reduced pressure. The distillate readily solidified on cooling, yield 1 g. The distillate was converted into picrate which crystallised from rectified spirit in orange needles, m. p. 119°-20°. The hydrocarbon was regenerated from the picrate and crystallised from methyl alcohol in plates, m. p. 53-54°. The mixed m. p. of the hydrocarbon with a sample of 2-methylaphenanthrene and that of its picrate with the picrate of 2-methylphenanthrene remained unaltered.

«(3′-Methyl*cyclo*pentane)-β-(*p*-toluyl)propionic acid (I, R=R′=Me) was prepared as described by Desai and Wali (*loc. cit.*). Its semicarbazone crystallised from dilute alcohol, m. p. 175-76° (decomp.). (Found : C, 64.1 ; H, 7.5. $C_{17}H_{23}O_3N_3$ requires C, 64.35 ; H, 7.25 per cent). This keto-acid gave «-(3′-methyl*cyclo*pentane)-γ-(*p*-tolyl)butyric acid (Desai and Wali, *loc. cit.*) on Clemmensen reduction.

1-*Keto*-7-*methyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*-2 : 2-*spiro*-(3′-*methyl*cyclo*pentane*) (III, R=R′=Me).—The butyric acid (III, R=R′=Me) (10 g.) was heated

on a steam-bath with 85% sulphuric acid (40 c. c.) for 1½ hours with stirring. The product was purified just as in the case of the ketone (III, R = H ; R' = Me). It is a colorless liquid with a characteristic odour, b. p. 160 – 161°/5 mm., yield 6 g. (Found : C, 83.8 ; H, 9.0. $C_{16}H_{20}O$ requires C, 84.2 ; H, 8.8 per cent).

The *oxime* of this spiro-ketone was obtained by heating it with hydroxylamine hydrochloride in pyridine solution for 6 hours. It crystallised from methyl alcohol in needles, m. p. 112-13°. (Found : C, 78.7 ; H, 8.7. $C_{16}H_{21}ON$ requires C, 79.0 ; H, 8.6 per cent).

7-*Methyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*-2 : 2-*spiro*-(3'-*methyl*cyclo*pentane*) (IV, R = R' = Me).—The spiro-ketone (III, R = R' = Me) (5.5 g.) was heated with amalgamated zinc (22 g.) and concentrated hydrochloric acid (22 c. c.) for 24 hours. The product was extracted with ether, washed, dried and distilled. It is a liquid, b. p. 135°-137°/5 mm., yield 4 g. (Found : C, 89.4 ; H, 10.4. $C_{16}H_{22}$ requires C, 89.7 ; H, 10.3 per cent).

Dehydrogenation of the Spiro-hydrocarbon (IV, R = R' = Me).—The spiro-hydrocarbon (3 g.) was heated with Pt-C catalyst (0.3 g.) in a metal-bath at 300°-310° for 6 hours and at 310°-320° for 6 hours when dehydrogenation was complete. The product was thoroughly extracted with ether and benzene and was distilled over sodium under reduced pressure. The first fraction collected at 170°-175°/5 mm. as a solid with a greenish fluorescence, yield 2 g. The second fraction was collected at a much higher temperature as a yellowish solid, yield 0.5 g.

(*a*). The first fraction was converted into picrate in alcoholic solution, and crystallised thrice from rectified spirit and the hydrocarbon was regenerated from the picrate. The hydrocarbon crystallised from rectified spirit as thin flakes, m. p. 140°. (Found : C, 93.1 ; H, 6.9. Calc. for $C_{16}H_{14}$: C, 93.2 ; H.6.8 per cent). The picrate prepared from the regenerated hydrocarbon was crystallised from rectified spirit in orange needles, m. p. 174°. Haworth records the m. p. of 3 : 6-dimethylphenanthrene as 140-41° and that of its picrate as 172-73° (*J. Chem. Soc.*, 1934, 460).

(*b*). The second fraction was twice crystallised from methyl alcohol and obtained in shining flakes with bluish fluorescence, m. p. 225°. The high m. p. of the product indicated that probably it was a mixture of 2 : 6-dimethyl - and 2 : 7-dimethylanthracene (cf. Morgan, *ibid.*, 1929, 2203). With the small amount of the material at our disposal, separation of the isomeric anthracenes could not be effected.

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PRECIPITATION OF ZINC HYDROXIDE WITH ALKALI AND ITS SOLUBILITY IN AQUEOUS AMMONIA

By K. S. Venkateswarlu

The product of gradual additon of alkali to a solution of zinc sulphate is first a basic salt accompanied by varying amounts of the hydroxide. When the amount of the alkali reaches the equivalence point, still a little sulphate is formed along with the hydroxide in the precipitate, due in all probability to adsorption. Experiments on the solubility of the zinc precipitate in aqueous ammonia indicates the variation of its solubility.

Bonsdorff (*Z. anorg. Chem.*, 1904, **41**, 185) and Euler (*Ber.*, 1903, **36**, 3400) have noted that the solubility of certain metallic hydroxides in ammonia solutions varies with conditions of precipitation. Dey and Ghosh (this *Journal*, 1947, **24**, 181) and Mehrotra and Ghosh (*Proc. Nat. Acad. Sci. India*, 1946, **15**, 161) found that the solubility of copper hydroxide depended on the quantity of alkali used for precipitation. Likewise Shaw and Ghosh (this *Journal*, 1950, **27**, 679) found similar dependence in the case of nickel hydroxide. It is shown in the present communication that zinc hydroxide exhibits a similar behaviour. It is further shown that the result of adding controlled amounts of alkali to the zinc sulphate solution is a preliminary precipitation of a basic sulphate together with varying amounts of the hydroxide.

Experimental

All reagents were of B. D. H. Analar quality. A stock solution of zinc sulphate was prepared. The zinc was estimated volumetrically by titration with ferrocyanide following the method of Cone and Caddy (*J. Amer. Chem. Soc.*, 1927, **49**, 356) as modified by Kolthoff ("Volumetric Analysis", Vol. II, p 256) and the sulphate gravimetrically, as barium sulphate.

From 50 c. c. samples of the stock solution zinc was precipitated at the room temperature (29.5 ± 0.5°) with the desired amount of 0.0887*N*-NaOH (carbonate-free). This precipitate was afterwards thoroughly shaken for half an hour and was filtered off and washed with cold distilled water. The amounts of zinc and sulphate in the filtrate and in the precipitate were estimated separately. The p_H of the solution was measured on duplicate samples without filtering, using buffers of Clark and Lub (Kolthoff and Laitinen, "p_H and Electro-titrations", p.35) in conjunction with suitable indicators.

The results of the p_H measurement and those of Zn and SO_4'' estimations are recorded in Table I.

TABLE I

Expt. No.	NaOH added.	% Equiv. of NaOH.	p_H of the mixture.	Amount of zinc in		Amount of SO_4'' in	
				ppt.	filtrate.	ppt.	filtrate.
1.	0 c.c.	0	5.8	0.0000 g.	0.8208 g.	0.0000 g.	1.207 g.
2.	2.85	10.05	5.9	0.1142	0.7084	0.0679	1.106
3.	5.65	19.93	6.0	0.2314	0.5887	0.1107	1.094
4.	8.5	29.97	6.2	0.337	0.4804	0.1547	1.021
5.	11.25	39.63	6.4	0.4512	0.3663	0.2025	1.002
6.	14.1	49.73	6.6	0.5769	0.2402	0.2272	0.9774
7.	16.9	59.61	6.8	0.686	0.1321	0.2782	0.9269
8.	19.75	69.65	7.0	0.7508	0.0682	0.3086	0.8961
9.	21.25	74.94	7.3	0.791	0.0267	0.3398	0.8656
10.	22.75	80.24	8.1	0.820	0.0000	0.3665	0.8381
11.	24.15	85.17	8.7	0.8166	,,	0.2669	0.9378
12.	25.4	89.58	9.2	0.8166	,,	0.2442	0.9603
13.	26.8	94.52	9.5	0.8200	,,	0.1743	1.031
14.	28.35	100.00	9.8	0.8269	,,	0.1095	1.095

These observations lead to the following interesting conclusions.

(*i*) The removal of zinc from solution is complete when about 80% equivalent of alkali is added.

(*ii*) The amount of sulphate held by the precipitate also increases up to this point, after which it begins to decrease.

(*iii*) The p_H of the solution rises up to this point, when it undergoes an irregular rise.

Thus, it appears that when sodium hydroxide is gradually added to zinc sulphate solution, zinc continuously separates from solution, both in the form of hydroxide and a basic salt. When all the zinc separates out (80% equivalence of alkali), further addition of alkali results in an attack on the basic salt which transforms it into the hydroxide. All the same, a small amount of sulphate is held tenaciously by the hydroxide (Adsorption expts. Nos. 12 to 14).

Solubility of the Zinc Precipitate in Ammonia.—To study this phenomenon, $Zn(OH)_2$ was made up with water to 250 c. c. in a volumetric flask and shaken for several hours to ensure uniform dispersion. Known volumes of this suspension were then shaken with a known volume of aqueous ammonia of the desired concentration, the volume of ammonia chosen being such as to leave a little undissolved residue. After standing overnight aliquot parts of the clear supernatant liquid were analysed for zinc. The results are shown in Table II.

TABLE II

Exp. No.	Amount of zinc (in g.) dissolved in 1000 c. c. of NH_4OH of				
	0.25 *N.*	0.5 *N.*	0.75 *N.*	1.00 *N.*	1.25 N.
	2	3	4	5	6
1.	...	There is no precipitate in this case.			
*2.	...	...	...	...	...
3.	0.2285	...	...	...	...
4.	0.2451	0.449	...	...	...
5.	0.2806	0.5941	0.9154	1.322	...
6.	0.3244	0.6913	1.154	1.714	1.885
7.	0.3256	0.7799	1.331	1.85	2.251
8.	0.3485	0.917	1.486	2.028	2.616
9.	0.4171	1.001	1.576	2.16	2.784
10.	0.4285	1.114	1.674	2.454	2.885
11.	0.3428	1.019	1.535	2.077	2.708
12.	0.2058	0.9199	1.473	1.886	2.603
13.	0.1199	0.8085	1.382	1.806	2.462
14.	0.0857	0.6886	1.307	1.701	2.731

*The blanks indicate that the amount of zinc present was not sufficient to form a saturated solution under the experimental conditions.

It is evident from Table II that the solubility of $Zn(OH)_2$ in NH_4OH varies. The maximum solubility is exhibited by that sample of the precipitate which is formed when about 80% of alkali required is employed (sample No. 10). As it is, these figures in themselves show no regular sequence, but more data may help to interpret these irregularities. Further work is in progress.

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STUDIES ON THE ACTIVE PRINCIPLES OF *SKIMMIA LAUREOLA*, HOOK

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An alkaloid, skimmianine ($C_{14}H_{15}O_4N$, m. p. 176-77°), three coumarins, viz. umbelliferone ($C_9H_6O_3$, m. p. 232°), bergapten ($C_{12}H_{10}O_4$, m. p. 188-90°) and *iso*pimpinellin ($C_{13}H_{10}O_5$, m. p. 150°), and a neutral compound, laureoline ($C_{24}H_{32}O_8$, m. p. 258-60°) have been isolated from the leaves and bark of *Skimmia laureola*, Hook.

Skimmia laureola, Hook, a common fodder plant of India, has been the subject of investigations by several workers (Roure-Bertrand, *Fils Bull.*, 1920, **34**, 2; *Schimmel. Ber.*, 1926, **46**, 3; Simonsen, *J. Soc. Chem. Ind.*, 1921, **40**, 126T; *Schimmel I. C. Constanten*, 1913, **72**, 5; Schimmel & Co. Rept. 1932, 5-73; Wienhaus and Rajdhan, *J. prakt. Chem.*, 1936, **147**, 113; Chopra, Chatterjee, Dey and Ghosh, *Indian J. Med. Res.*, 1938, **26**, 481) for the past few years. The presence of an alkaloid, skimmianine, $C_{14}H_{13}O_4N$ (I, m. p. 176-77°), a furocoumarin bergapten, $C_{12}H_{10}O_4$ (II, m. p. 188-90°), a neutral substance, skimmiol (m. p. 279-81°) and essential oils have been reported to be present in the leaves of this plant.

During the isolation of skimmianine (I) from the leaves of this plant for preparing its authentic sample, it has been observed by the present authors that the leaves of *Skimmia laureola* contain three more active ingredients which have not been recorded so far, by the previous workers. One of these constituents is *iso*pimpinellin ($C_{13}H_{10}O_5$, m. p. 150°), a dimethoxyfurocoumarin; the second one is umbelliferone, a 7-hydroxycoumarin ($C_9H_6O_3$, m. p. 232°, yield, 0.1%) and the third compound is laureoline, a neutral substance ($C_{24}H_{32}O_8$, m. p. 258-60°, yield 0.02%) which appears to be hitherto unknown. The bark of this plant has also been investigated and five crystalline constituents, viz., the alkaloid skimmianine, three coumarins and the same neutral compound, laureoline, have been isolated, the properties and constitution of which are described herein.

Skimmianine, $C_{11}H_{14}ON(OCH_3)_3$ (yield 0.05%), the optically inactive, weak and tertiary base (which distils unchanged in vacuum at 150°/0.1 mm.) was obtained on basification of the acid digest of the ethereal extract of the powdered bark of *Skimmia laureola*.

The sodium carbonate digest of the residual solution precipitated umbelliferone (yield 0.1%) on acidification.

The neutral ether extract of the bark deposited laureoline. It does not give any coloration with ferric chloride. It is insoluble in alkali and does not produce any characteristic coloration with steroidal reagents. Laureoline dissolves in concentrated sulphuric acid with a yellow colour. It is free from methoxy and methylene-dioxy groups. Further work on the elucidation on the structure of laureoline is in progress which will be reported later.

A mixture of bergapten (yield 0.3%) and *iso*pimpinellin (yield 0.005%) was obtained from the saponifiable portion of the neutral extract.

EXPERIMENTAL

Air-dried powdered leaves of *Skimmia laureola* (800.0 g.) were soxhletted with ether (2 litres) for 48 hours. The greenish brown ethereal extract was shaken with 0.1% hydrochloric acid (300 c. c. in three instalments) when skimmianine passed into the acid layer. The brown, non-basic ether solution (P) was kept aside, and the brown acid extract (Q) was worked up for the isolation of skimmianine.

Isolation of Skimmianine from (Q).—The acid aqueous solution (Q ; *vide supra*) was cooled in ice water and basified with sodium bicarbonate. The base separating was taken up in chloroform (100 c. c.), washed with water, dried over anhydrous sodium sulphate and distilled. The residue (0. 4 g.), left on removal of the solvent, crystallised from ethyl acetate in colorless prisms, m. p. 176-77°. On repeated crystallisations from ethanol, acetone and ethyl acetate, the m. p. remained unchanged. (Found : C, 65.06 ; H, 4.86 ; N, 5.51 ; OMe, 36.02. Calc. for $C_{14}H_{13}O_4N$: C, 64.86 ; H, 5.02 ; N, 5.41 ; OMe, 35.96 per cent).

The *picrate* was prepared by adding an ethereal solution of picric acid to an ethereal solution of skimmianine. The yellow precipitate crystallised from alcohol in yellow plates, m. p. 193-94° (decomp.). [Found : N, 11.29. Calc. for $C_{14}H_{13}O_4N$, $C_6H_2OH(NO_2)_3$: N, 11.48 per cent].

The *chloroplatinate* was prepared by adding an aqueous solution of platinic chloride (5%) to a faintly hydrochloric acid solution of skimmianine. Upon crystallisation from water containing a little hydrochloric acid glistening orange coloured plates were obtained, which did not melt but charred at 200°. [Found : Pt, 20.82, 20.68. Calc. for $(C_{14}H_{13}O_4N)_2$, H_2PtCl_6 : Pt, 21.01 per cent].

Isolation of Umbelliferone from the fraction (P).—The non-basic, brown ether solution (P) was digested with an aqueous solution of sodium carbonate (2*N*, 100 c. c.) when umbelliferone was dissolved out of the ether layer into the carbonate solution (Q′) which exhibited a deep violet fluorescence. The neutral ether portion left was washed with water, dried over anhydrous sodium sulphate, concentrated to a small bulk (P′) and kept in the frigidaire. The carbonate solution (Q′ ; *vide supra*) was acidified with hydrochloric acid when umbelliferone separated. It was taken up with ether and the ethereal solution was washed with water, dried and freed from the solvent. The residue crystallised from ethyl acetate in glistening needles, m. p. 232° and showed no depression in m. p. when mixed with synthetic umbelliferone. (Found : C, 66.30 ; H, 3.88. Calc. for $C_9H_6O_3$: C, 66.67 ; H, 3.70 per cent).

Methylation of umbelliferone was effected by refluxing an acetone solution (dried over potassium carbonate) of it with freshly distilled methyl iodide in presence of potassium carbonate for 6 hours. It crystallised from methanol in colorless needles,

m. p. 119° and showed no change in m. p. when admixed with synthetic methylumbelliferone. [Found : OMe, 17.63. Calc. for $C_9H_5O_2$ (OCH_3) : OMe, 17.62 per cent].

Isolation of Laureoline from the fraction (P').—The neutral ethereal extract (P') on keeping in the frigidaire deposited laureoline after four weeks. Laureoline was collected and separated from the adhering gum by washing with ether. It crystallised from ethanol and acetone in rhombic plates, m. p. 258-60°. [Found : C, 63.80 ; H, 7.21 ; M. W. (by Rast's method), 440, 436. Calc. for $C_{24}H_{32}O_8$: C, 64.28 ; H, 7.14 per cent. M. W., 448].

The neutral extract left after the separation of laureoline was freed from the solvent and the oil obtained was worked up by the method of Späth and Socias (*Ber.*, 1934, **67**, 59) for the isolation of bergapten and *iso*pimpinellin. The oil was cooled to about 15° and to it was added 200 c. c. of 20% methyl alcoholic potassium hydroxide solution with constant stirring. The mixture was allowed to stand for 45 minutes, then poured into one litre of ice water and the aqueous solution was extracted with ether to remove non-saponifiable portions. The reddish brown aqueous alkaline solution was acidified with hydrochloric acid (Congo red) and allowed to stand overnight. Next morning the greater portion of methyl alcohol was removed under reduced pressure, then cooled and thrice extracted with ether (300 c. c.). The ether digest was washed with an aqueous solution of potassium carbonate (100 c. c., 25%), then with water and finally dried over anhydrous sodium sulphate. The residue left on removal of the solvent solidified on keeping in a frigidaire for a week. The solid (R) was washed with light petrol (b. p. 40°-60°) when glistening yellow needles mixed up with shining, colorless needles were obtained.

Isolation of Bergapten and iso*Pimpinellin from the fraction (R).*—The fraction (R ; *vide supra* ; yield, 3.2 g.) was thrice crystallised from methanol when colorless, silky needles of bergapten of m.p. 184-86° separated. These were collected and the mother-liquor (R') was kept for further investigation. Crude bergapten, m.p. 184-86° (2.0g) distilled at 150-55°/0.1 mm. The colorless distillate quickly solidified and was recrystallised from ethyl acetate and methanol when m. p. could be raised to 188-90°. [Found : C, 67.06 ; H, 4.03 ; OMe, 14.40. Calc. for $C_{11}H_5O_3(OCH_3)$: C, 66.67 ; H, 3.70 ; OMe, 14.35 per cent].

The sample showed no depression in m.p. when mixed with a pure sample of bergapten.

Isolation of iso*Pimpinellin from R'.*—The mother-liquor (R' ; *vide supra*) on removal of the solvent was distilled in high vacuum when two different fractions were obtained. The first fraction (A) (yield 0.04 g.) was collected at 115°-120°/0.1 mm. and the second (B) (yield 0.4g.) at 150°-155°/0.1 mm. The fraction (A) crystallised from ethyl acetate, methanol and 50% ethyl alcohol in yellow glistening needles, m.p. 150°. It showed no change in m.p. when mixed with an authentic sample of *iso*pimpinellin. [Found : C, 62.92 ; H, 3.89 ; OMe, 24.86. Calc. $C_{11}H_4O_3(OCH_3)_2$: C, 63.41 ; H, 4.06 ; OMe, 25.2 per cent].

The second fraction of the distillate was crystallised from alcohol when silky needles of bergapten, m.p. 188-190° separated. Its m.p. remained unchanged when mixed with an authentic sample of bergapten.

The same experimental procedure (described above) has been followed for the isolation and identification of active principles of the bark of *S. laureola*.

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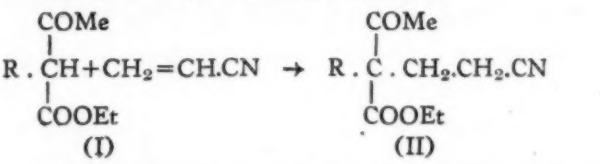
PREPARATION OF SOME MONOCYANOETHYLATED KETONES

By G. S. Misra and J. S. Shukla

The ketonic hydrolysis of an ethyl α-alkyl-α-(2-cyanoethyl)acetoacetate results in the formation of an α-(2-cyanoethyl)ketone.

Ketones, which have a methinyl, methylene or methyl group contiguous to the carbonyl group, react with acrylonitrile with the formation of a mono-, di-, tri- or even a poly-cyanoethylation product. Thus, acetone reacts with acrylonitrile to yield a small quantity of a monocyanoethylation product $CH_3COCH_2CH_2CH_2CN$, but the reaction mainly gives the tricyanoethylation product $CH_3CO.C(CH_2CH_2CN)_3$ (Bruson and Riener, *J. Amer. Chem. Soc.*, 1942, **64**, 2850). An unsymmetrical aliphatic ketone, like methylethyl ketone, on the other hand, reacts with acrylonitrile under appropriate conditions to yield a product where the methylene group has been dicyanoethylated in preference to a methyl group (Bruson and Riener, *loc. cit.*). It will be observed that in the above cases, the reaction with acrylonitrile does not stop at the stage of monocyanoethylation.

The reaction between acrylonitrile and monoalkylated acetoacetic esters (Misra and Shukla, this *Journal*, 1952, **29**, 455) has now been utilised to furnish a general route for the synthesis of the α-(2-cyanoethyl)ketones. In this method the resulting α-alkyl-α-(2-cyanoethyl) acetoacetate is submitted to *ketonic hydrolysis* to furnish the α-(2-cyanoethyl)ketone, thus :



(I) (II) (III)

It was found that when the cyanoethylation product (II) was heated with 5% potassium hydroxide, the *ketonic hydrolysis* had not taken place to any appreciable extent. When, however, the product (II) was heated with 10% potassium hydroxide for about five hours, extraction of the resulting mixture with ethylene dichloride and evaporation of the ethylene dichloride extract furnished the desired monocyanoethylated ketone. The yields of the ketones were 30.6 to 43.4% only.

Experimental

Preparation of Ethyl-α-Alkyl-α-(2-cyanoethyl)acetoacetates.—These compounds were prepared in accordance with the method already described (Misra and Shukla, *loc. cit.*).

Preparation of Monocyanoethylated Ketones : 3-(*β-Cyanoethyl*)-2-*butanone.*—Ethyl α-methyl-α-(2-cyanoethyl)acetoacetate (11 g.) was heated on a waterbath with 10% potassium hydroxide (50 c. c.) for five hours. The mixture was cooled and

extracted with ethylene dichloride several times. The ethylene dichloride layer was washed several times with water till it ceased to react alkaline to litmus paper. It was then allowed to stand over anhydrous magnesium sulphate overnight, and the ethylene dichloride evaporated off under reduced pressure. The residual oil was fractionally distilled under reduced pressure. The fraction of b. p. 93°/8 mm. was collected, yield 2.4 g. (34.4%). (Found : N, 10.8. $C_7H_{11}ON$ requires N, 11.2 per cent.).

The other monocyanoethylated ketones have been prepared similarly. They are described in Table I.

TABLE I

**R =	Monocyanoethylated ketone formed.	Yield.	B. P.	Formula.	% Nitrogen Calc.	% Nitrogen Found.
Methyl	3-(β-C*)-2-butanone	34.4%	93/8 mm.	$C_7H_{11}ON$	10.8	11.2
Ethyl	3-(β-C)-2-pentanone	43.4	114/12	$C_8H_{13}ON$	9.5	10.07
n-Propyl	3-(β-C)-2-hexanone	36.2	110/5-6	$C_9H_{15}ON$	8.4	9.15
n-Butyl	3-(β-C)-2-heptanone	34.8	117/6-7	$C_{10}H_{17}ON$	8.0	8.38
n-Amyl	3-(β-C)-2-octanone	31.9	120/8	$C_{11}H_{19}ON$	7.2	7.7
Benzyl	3-(β-C)-4-phenyl--2-butanone	30.6	95/5	$C_{13}H_{15}ON$	6.8	6.96

*C-denotes cyanoethyl.

**R = α-alkyl-α-(2-cyanoethyl) acetoacetate.

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VARIATION OF ELECTRICAL CONDUCTANCE WITH CONCENTRATION OF AQUEOUS SODIUM OLEATE SOLUTIONS IN PRESENCE OF DIFFERENT CONCENTRATIONS OF ALCOHOLS AND SALT

By A. N. Bose

Variation of specific conductance of sodium oleate—water with varying concentrations of alcohols has been studied. The results have been explained on the basis of the structure that alcohol molecules arrange themselves in the palisadel layers of oleate molecules.

Electrical conductance of solutions of long chain salts in the presence of methyl and ethyl alcohols has been studied by Ward (*J. Chem. Soc.*, 1939, 522), Grieger and Kraus (*J. Amer. Chem. Soc.*, 1948, **70**, 380), Rollston and Egerberger (*ibid.*, 1948, **70**, 983) and Brown, Grieger aud Kraus (*ibid.*, 1949, **71**, 95). It has been found by Brown and co-workers that the behaviour of *iso*propyl alcohol and *tert.*-butyl alcohol is different from that of methyl and ethyl alcohols. The present work has been undertaken with a view to ascertaining if the variation in the concentration of alcohols changes the structure of 0.4*N*-sodium oleate solution in water.

Experimental

Experimental method is the same as recorded in the previous communication (this *Journal*, 1952, **29**, 135). Results obtained are shown in Table I. Electrical conductance has been studied in most of the cases at five different concentrations and temperatures but the results have been reported only at two temperatures.

Table I

Variation of specific conductance with concentration ($\mu \times 10^2$)

Conc. of Na-oleate in all the solutions = 0.4 *N*.

Temp.	In absence of NaCl.	Concentration of NaCl solution. *N*/1.	*N*/20.	*N*/40.	*N*/80.	*N*/160.
		10% *n*-Propyl alcohol.				
30°	1.500	2.174	1.841	1.675	1.582	...
50°	2.293	3.227	2.783	2 527	2.400	...
		20% *n*-Propyl alcohol.				
30°	1.300	1.870	1.662	1.470	1 404	1.374
50°	2.004	2.773	2.451	2.250	2.133	2 092
		30% *n*-Propyl alcohol.				
30°	1.042	1.485	1.272	1.158	1.114	...
50°	1.536	2.293	1.950	1.815	1.733	...

TABLE I (*contd.*)

Temp.	In absence of NaCl.	Concentration of NaCl solution. *N*/1.	*N*/20.	*N*/40.	*N*/80.	*N*/160.
		40% *n*-Propyl alcohol.				
30°	0.8144	...	0.9845	0.9125	0.8340	0.8531
50°	1.2800	...	1.4930	1.4270	1.3630	1.3400
		50% *n*-Propyl alcohol.				
30°	0.5984	...	0.6431	0.6391	...	...
50°	0.9418	...	1.0920	1.0050	...	...
		10% *iso*Propyl alcohol.				
30°	1.3660	2.107	1.723	1.493	1.419	1.388
50°	2.126	3.107	2.680	2.400	2.212	2.167
		20% *iso*Propyl alcohol.				
30°	1.183	...	1.435	1.353	1.242	1.243
50°	1.908	...	2.293	2.138	2.017	1.990
		30% *iso*Propyl alcohol.				
30°	0.9460	...	1.1620	1.096	1.040	1.000
50°	1.5860	...	1.9090	1.774	1.692	1.635
		40% *iso*Propyl alcohol.				
30°	0.7568	...	0.8900	0.8350	0.7871	...
50°	1.2300	...	1.4600	1.3570	...	...
		50% *iso*Propyl alcohol.				
30°	0.5688	...	...	...	...	...
50°	0.9140	...	...	...	...	...
		10% *n*-Butyl alcohol*.				
30°	1.551	2.202	1.893	1.706	1.640	1.614
45°	2.116	2.977	2.567	2.352	2.244	2.208
		20% *n*-Butyl alcohol*.				
30°	1.246	1.724	1.487	1.357	1.328	1.272
45°	1.676	2.342	2.017	1.866	1.811	1.743
		30% *n*-Butyl alcohol*.				
30°	0.8866	1.180	1.036	0.9687	0.9347	...
45°	1.2110	1.592	1.410	1.3160	...	...

TABLE I (*contd.*)

Temp.	In absence of NaCl.	Concentration of NaCl solution. *N*/1	*N*/20.	*N*/40.	*N*/80.	*N*/160.
		40% *n*-Butyl alcohol*.				
30°	0.5425	...	0.7278	0.6283	0.5696	...
45°	0.7633	...	0.5173	0.8561	0.7923	...
		50% *n*-Butyl alcohol*.				
30°	0.2375	...	...	0.2438	...	...
45°	0.3466	...	...	0.3637	...	...
		10% *n*-Amyl alcohol.				
30°	1.641	...	1.945	1.787	1.720	1.643
45°	2.219	...	2.614	2.407	2.221	2.193
		30% *n*-Amyl alcohol.				
30°	0.8806	...	0.8858	0.8874	0.8883	...
50°	1.3850	...	1.4620	1.4460	1.4310	...
		40% *n*-Amyl alcohol.				
30°	0.7066	...	...	...	...	...
50°	0.8872	...	...	...	...	...
		50% *n*-Amyl alcohol.				
30°	0.2703	...	...	...	...	...
50°	0.4903	...	...	...	...	...

*In the case of *n*-butyl alcohol 10, 20, 30, 40 and 50 g. of alcohol were dissolved in 100 c.c. of solution. In some cases addition of NaCl separated the alcohol and water layer.

DISCUSSION

From the results in Table I, specific conductance was plotted against the concentration of sodium chloride for each concentration of alcohol, for example in the case of 10% *n*-propyl alcohol the concentrations of sodium chloride taken up were *N*/20, *N*/40, *N*/80 and *N*/160. The specific conductance was plotted against these concentrations of sodium chloride. In the case of lower concentration of *iso*propyl and *n*-propyl alcohol, the plot of μ-c shows curvature. Probably this is due to the fact that alcohol and water molecules form hydrates and these hydrated molecules are broken up by the addition of sodium chloride and the degree of breaking up of hydrated molecules depends on the concentration of sodium chloride as a result of which the plot of μ-c shows a curvature. It is further observed that above and below *N*/40 sodium chloride concentration the nature of the curve is

different; this is due to the fact that at $N/40$ sodium chloride concentration the hydration is just completely broken up and below this concentration the hydration is not broken up. Similar results have been obtained in the case of viscosity, where it has been observed that at $N/40$ sodium chloride concentration the viscosity is minimum due to the complete breaking up of the hydrated molecules.

It has been further observed that at higher concentrations of alcohol the plot of μ-c does not show so much of curvature as at lower concentrations. This may be due to the fact that at higher concentrations of alcohol, the alcohol molecules replace the water molecules present in between the two layers of oleate molecules as a result of which hydration decreases.

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POSSIBLE ANTI-TUBERCULAR COMPOUNDS. PART II. PREPARATION OF ACYLDIPHENYLYLAMIDINES

By Vinay S. Misra and Maheshwari P. Khare

With a view to further increasing the surface area of 4-aminodiphenyl compound of known anti-tubercular activity, seven higher 4′-acyldiphenylylamidines have been prepared.

In Part I this series (Misra and Khare, this *Journal*, 1952, **29**, 695) a series of 4′-aceto-4-N-diphenylylamidines have been described, the starting material being 4-aminodiphenyl, a strongly anti-tubercular compound.

In the present paper we have tried to further increase the surface area of N-4-diphenylylamidines by introducing the lipoid-soluble propionyl and *n*-butyryl groups in the 4′-position of the 4-aminodiphenyl instead of the acetyl, and subsequently preparing seven new amidines by the usual method of Oxley and Short (*J. Chem. Soc.*, 1949, 147), adopted by us in the previous case.

The 4′-propio-4-aminodiphenyl was prepared by us by the application of the Friedel-Crafts reaction. The Friedel-Crafts reaction was conducted in the presence of dry carbon disulphide with 2.5 moles of anhydrous aluminium chloride when the intermediate 4′-propio-N-4-propioacetaminodiphenyl, as expected from the analogous aceto series (Misra and Khare, *loc. cit.*) was obtained in excellent yields. In the case of the butyro series, instead of the diacyl compound, 4′-butyro--N-4-acetaminodiphenyl was obtained, as confirmed by its nitrogen content and that of its 2 : 4-dinitrophenylhydrazone.

The respective free amines were liberated by the hydrolysis of the corresponding acylamines with concentrated hydrochloric acid.

The Friedel Crafts reaction was also conducted in the presence of dry nitrobenzene as in the previous paper, but in this case, contrary to our expectations, the ketone synthesis and the hydrolysis of the intermediate product proceeded simultaneously, and the free amine could only be obtained in very poor yields as a considerable amount of a tarry product was also produced.

These amines were converted into the corresponding benzene sulphonate in the manner described in the earlier communication (*loc cit.*).

I. $R = C_2H_5$ R.CO– –NH_2 $\xrightarrow{Ph\,SO_3H}$

R.CO– –$\overset{+}{N}H_2.C_6H_5SO_3\overset{-}{H}$

II. $R = C_3H_7$.

These benzene sulphonates (I & II) were then fused at 220°-230° with excess of *o*-, *m*- and *p*-tolyl and *p*-aniso-nitriles respectively, and the appropriate amidine-benzene sulphonates were obtained.

The free amidines (in 28 to 68% yield) were liberated by treating the benzene sulphonates with 5*N*-sodium hydroxide and were recrystallised from chloroform and petroleum ether except the 4′-butyro-N-4-diphenyl-*o*-tolylamidine which, however, could not be obtained in a pure form in spite of repeated attempts.

The anti-tubercular activity of the amidines will be reported latter on.

Experimental

4′-*Propio*-N-4-*propioacetaminodiphenyl* (I).—Anhydrous aluminium chloride (2.5 *M*, 30 g.) was added to 4-acetaminodiphenyl (16 g.), suspended in dry CS_2 (40 g.) in a 500 c. c. R. B. flask fitted with a reflux condenser having a calcium chloride tube and a dropping funnel at its top. Now, to the cooled mixture propionyl chloride (3.5 *M*, 18 g.) was added dropwise when the reaction proceeded briskly with the evolution of gaseous HCl. After the evolution of HCl had slowed down the product was refluxed for half an hour on a water-bath to complete the reaction. The CS_2 was then distilled off and the resulting complex, a green paste, was decomposed with crushed ice and dilute HCl. The resulting yellow powder was filtered and recrystallised from glacial acetic acid, m. p. 226-27°, yield 53% of theory (12.3 g.). (Found : N, 5.0. $C_{20}H_{21}O_3N$ requires N, 4.34 per cent).

The 2 : 4-*dinitrophenylhydrazone* of the above was recrystallised from nitrobenzene as a red powder, m. p. 266-68°. (Found : 13.77. $C_{26}H_{25}O_6N_5$ requires N, 13.90 per cent).

4′-*Butyro*-N-4-*acetaminodiphenyl* (II).—Anhydrous aluminium chloride (2.5 *M*, 30 g.) was added to 4-acetaminodiphenyl (16 g.), suspended in dry CS_2 (40 g.). Butyryl chloride (3.5 *M*, 20 g.) was added dropwise under cooling. The subsequent treatments were similar to the previous compound (I). The resulting powder was filtered and recrystallised from alcohol as a yellow crystalline powder, m. p. 209°, yield 70% of theory (14 g.). (Found : N, 5.30. $C_{18}H_{19}O_2N$ requires N, 4.98 per cent).

The 2 : 4-*dinitrophenylhydrazone of* (II) was recrystallised from nitrobenzene as red crystals, m. p. 262-63°. (Found : N, 15.30. $C_{24}H_{23}O_5N_5$ requires N, 15.19 per cent).

4′-*Propio*-4-*aminodiphenyl* (III).—4′-Propio-N-4-propioacetaminodiphenyl (12.3 g.) was hydrolysed with HCl (conc., 50 c. c.) by refluxing for four hours and the product neutralised with concentrated ammonia when a yellow mass was obtained. This on recrystallisation from 80% alcohol gave a yellow amorphous powder, m. p. 168-69°, yield 93% of theory (8 g.). (Found : N, 5.70. $C_{15}H_{15}ON$ requires N, 6.22 per cent).

The 2 : 4-*dinitrophenylhydrazone of* (III) was recrystallised from nitrobenzene as red powder, m. p. 231-32°. (Found : N, 16.93. $C_{21}H_{19}O_4N_5$ requires N, 17.28 per cent).

4'-Butyro-4-aminodiphenyl (IV).—4'-Butyro-N-4-acetaminodiphenyl (14 g.) was hydrolysed with HCl (50 c. c., conc.) and neutralised with ammonia (conc.). The precipitated powder was recrystallised from alcohol as brown needles, m. p. 116-17°, yield 94% of theory (9 g.). (Found : N, 6.15. $C_{16}H_{17}ON$ requires N, 5.86 per cent).

The 2:4-*dinitrophenylhydrazone* of (IV) was recrystallised from nitrobenzene as a red shining crystals, m. p. 253°. (Found : N, 17.10. $C_{22}H_{21}O_4N_5$ requires N, 16.71 per cent).

4'-Propio-4-diphenylylammonium-benzene sulphonate (A).—4'-Propio-4-aminodiphenyl (1 *M*, 7 g.) was stirred mechanically in 200 c. c. of dry ether and benzene sulphonic acid (1 *M*, 5 g.), dissolved in 10 c. c. of methyl alcohol, was added slowly. A white paste was formed which was filtered and recrystallised from hot water as a pale yellow powder, m. p. 244-46°, yield 42% of theory (5 g.). (Found : N, 4.10. $C_{21}H_{21}O_4NS$ requires N, 3.65 per cent).

4'-Butyro-4-diphenylylammonium-benzene sulphonate (B).—To 4'-butyro-4-aminodiphenyl (1 *M*, 8 g.) stirred in 200 c. c. dry ether, benzene sulphonic acid (1 *M*, 5 g.), dissolved in methyl alcohol, was added dropwise. The benzene sulphonate separated out and was filtered and recrystallised from 30% alcohol as a white amorphous powder, m. p. 257-60°, yield 68% of theory (9 g.). (Found : N, 3.76. $C_{22}H_{23}O_4NS$ requires N, 3.52 per cent).

4'-Propio-N-4-diphenylyl-o-tolylamidine.—The compound (A) (2.5 g.) was mixed with *o*-tolylnitrile (2.5 g.) in a 100 c. c. flask fitted with a reflux condenser and a gas absorption tower. The mixture was heated at 220°-230° (external bath temperature) for 4 hours. The pasty product formed was triturated with ether and a yellow amorphous powder of amidinebenzene sulphonate was obtained which was then stirred mechanically in 100 c. c. of 5*N*-NaOH for 6 hours and filtered. The resultant amidine was then recrystallised from chloroform and petroleum ether to give a dark brown solid, m. p. 125-30°, yield 59% of theory (1.3 g.). (Found : N, 7.70. $C_{23}H_{22}ON_2$ requires N, 8.18 per cent).

4'-Propio-N-4-diphenylyl-m-tolylamidine.—The compound (A) (2 g.) was heated with *m*-tolylnitrile (2 g., excess) for 4 hours at 220°-230°. The amidine was liberated as above as a yellow amorphous powder, m. p. 175-79°, yield 28% of theory (0.5 g.). (Found : N, 7.61. $C_{23}H_{22}ON_2$ requires N, 8.18 per cent).

4'-Propio-N-4-diphenylyl-p-tolylamidine was obtained by refluxing the mixture of (A) (2.5 g.) and *p*-tolylnitrile (4 g.) at 220°-225° for 6 hours as a yellow powder, m. p. 178-82°, yield 40% of theory (0.9 g.). (Found : N, 7.55. $C_{23}H_{22}ON_2$ requires N, 8.18 per cent).

4'-Propio-N-4-diphenylyl-p-anisoylamidine was similarly obtained as above by heating (A) (2.5 g.) with *p*-anisonitrile (5 g., excess) at 230° for 4 hours, m. p. 180°-82°, yield 43% of theory. (1 g.). (Found : N, 7.30. $C_{23}H_{22}O_2N_2$ requires N, 7.81 per cent).

4'-*Butyro*-N-4-*diphenylyl*-m-*tolylamidine.*—The compound (B) (2.5 g.) was heated with *m*-tolylnitrile (3 g.) for 4 hours at 230° under reflux. The amidine was obtained as a brown solid in the usual manner, m. p. 148-53°, yield 68% of theory (1.5 g.). (Found : N, 7.25. $C_{24}H_{24}ON_2$ requires N, 7.86 per cent).

4'-*Butyro*-N-4-*diphenylyl*-p-*tolylamidine* was similarly obtained by heating from (B, 2.5 g.) and *p*-tolylnitrile (3 g.) at 220° for 4 hours as a yellow amorphous powder, m. p. 181-85°, yield 54% of theory (1.2 g.). (Found : N, 7.65. $C_{24}H_{24}ON_2$ requires N, 7.86 per cent).

4'-*Butyro*-N-4 *diphenylyl*-p-*anisoylamidine.*—The compound (B) (2.5 g.) was mixed with *p*-anisonitrile (3.5 g.) and heated at 230° for 5 hours. The yellow amorphous amidine was liberated in the usual manner and melted at 156-60°, yield 42% of theory (1.4 g.). (Found : 7.75. $C_{24}H_{24}O_2N_2$ requires N, 7.53 per cent).

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MOLECULAR POLARISATION IN SOLIDS

By K. D. Pathak and B. V. Bhide

Dielectric constants of salts of alkalies and alkaline earths with straight chain aliphatic acids have been determined. Molecular polarisation calculated according to the Clausius-Mosotti equation has been found to be additive in sodium, potassium and barium salts of monobasic acids and in sodium salts of dibasic acids. Calcium salts show marked deviations. In all the series of salts molecular volume has been found to be additive.

A survey of the theories of dielectrics shows that there is no generalised theory of the dielectric properties of salts or solids in general. The previous work done on the subject has been in most cases related to the role of water in hydrates (Cheng, *Phil. Mag.*, 1940, **30**, 505), or changes in allotropic forms. The rest of the work is mainly concerned with the determination of dielectric constants of salts and interpreting them qualitatively in terms of the ionic and non-polar bonds. In the absence of a generalised theory, it was thought desirable to study the effect of organic radicals on the dielectric properties of inorganic ions. Such a scheme is easily available if one considers the inorganic salts of straight chain aliphatic acids. The aliphatic part of the acid is mostly non-polar and the effect of the addition of this component on the inorganic cation can be easily studied.

Experimental

Some of the acids required for the preparation of these salts were available in the laboratory. The remaining had to be prepared. Formic, acetic and butyric acids were redistilled before use. For the preparation of the salts of heptylic acid, first heptaldehyde was obtained by fractional distillation of castor oil which was further oxidised to heptylic acid by potassium permanganate. Lauric acid was obtained from Pisa seeds (*Actinodaphne hookeri*) and further distilled under reduced pressure. Stearic acid was obtained from Coccum butter (*Purpura*). It was obtained in the purest form after three crystallisations from ethyl alcohol, m. p. 71.5°.

The salts were prepared by standard methods. They were purified by crystallisation from water or alcohol, wherever possible. The salts were dried to a constant weight and were further analysed by standard methods to test their purity. In every case the purity was found to be over 99.5%.

Measurement of Dielectric Constants and Densities.—The dielectric constants were measured by the resonance method at 100 meter wave-length. The mixture method was used for determining the dielectric constants of solids. The liquids used for this method were xylene and nitrobenzene; for density measurements benzene was used.

Xylene was dried over sodium and then distilled twice over phosphorus pentoxide. Merck's pure thiophene-free benzene, distilled over phosphorus pentoxide, was further dried over sodium ; nitrobenzene was dried over calcium chloride and then distilled under reduced pressure.

All the density measurements were carried out at 30°. All the weights were corrected for buoyancy of air.

Table I gives the dielectric constant ϵ, density d, molecular polarisation P, and the molecular volume of salts. P is calculated according to Clausius-Mosotti equation

$$P = \frac{\epsilon-1}{\epsilon+2} \cdot \frac{M}{d}.$$

TABLE I

	Salt.	Formula.	ϵ.	d (g./c.c.).	P.	Mol. vol (M/d).
1.	Sodium formate	CHO_2Na	4.85	1.925	19.86	35.33
2.	Sodium acetate	$C_2H_3O_2Na$	4.44	1.518	28.87	54.03
3.	Sodium butyrate	$C_4H_7O_2Na$	3.825	1.324	40.29	83.08
4.	Sodium heptylate	$C_7H_{13}O_2Na$	3.61	1.204	58.73	126.3
5.	Sodium laurate	$C_{12}H_{23}O_2Na$	3.24	1.102	86.12	201.5
6.	Sodium stearate	$C_{18}H_{35}O_2Na$	3.125	1.07	118.4	286.0
1.	Sodium oxalate	$C_2O_4Na_2$	6.1	2.888	36.88	46.39
2.	Sodium malonate	$C_3H_2O_4Na_2$	5.6	2.08	43.07	71.15
3.	Sodium succinate	$C_4H_6O_4Na_2$	5.01	1.88	51.6	86.16
4.	Sodium adipate	$C_6H_8O_4Na_2$	4.14	1.66	58.3	114.5
5.	Sodium azealate	$C_9H_{14}O_4Na_2$	4.16	1 45	82.08	160.0
1.	Potassium formate	CHO_2K	7.46	1.954	29.36	42.99
2.	Potassium acetate	$C_2H_3O_2K$	4.61	1.534	34.89	63.89
3.	Potassium butyrate	$C_4H_7O_2K$	3.9	1.315	47.1	95.88
4.	Potassium laurate	$C_{12}H_{23}O_2K$	2.81	1.136	78.84	209.50
5.	Potassium stearate	$C_{18}H_{35}O_2K$	2.65	1.12	102.1	287.00
1.	Barium formate	$Ba(HCO_2)_2$	7.9	3.179	49.85	71.53
2.	Barium acetate	$Ba(C_2H_3O_2)_2$	5.62	2.47	62.67	103.4
3.	Barium butyrate	$Ba(C_4H_7O_2)_2$	4.55	1.875	89.89	166.2
4.	Barium heptylate	$Ba(C_7H_{13}O_2)_2$	3.62	1.568	117.6	252.2
5.	Barium laurate	$Ba(C_{12}H_{23}O_2)_2$	3.1	1.345	163.9	398.1
6.	Barium stearate	$Ba(C_{18}H_{35}O_2)_2$	2.815	1.244	213.2	265.4
1.	Calcium formate	$Ca(HCO_2)_2$	6.825	1.959	43 81	66.36
2.	Calcium acetate	$Ca(C_2H_3O_2)_2$	6.3	1.509	66.88	104.7
3.	Calcium butyrate	$Ca(C_4H_7O_2)_2$	4.9	1.271	95.23	168.4
4.	Calcium heptylate	$Ca(C_7H_{13}O_2)_2$	4.29	1.2	123 9	248.3
5.	Calcium stearate	$Ca(C_{18}H_{35}O_2)_2$	2.82	1.065	214.9	569.0

DISCUSSION

From the results the following deductions can be made.

Densities.—Fig. 1 shows the densities of the salts against the number of carbon atoms in the molecule. In every series of salts a smooth curve is obtained. The decrease in density with increase in carbon atoms is particularly prominent from formates to butyrates in the salts of monobasic acids where the increment in molecular weight represents a large proportion of the total. It is interesting to note that the curves of sodium and potassium salts of monobasic acids almost superimpose each other showing that the corresponding salts have nearly the same densities. No irregularity is observed in the values of the densities in these series of salts with odd and even number of carbon atoms.

Fig. 1

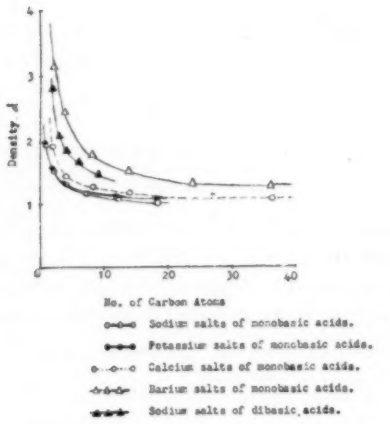
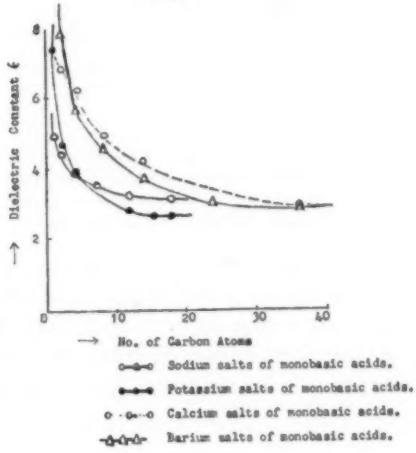

Density d
No. of Carbon Atoms
Sodium salts of monobasic acids.
Potassium salts of monobasic acids.
Calcium salts of monobasic acids.
Barium salts of monobasic acids.
Sodium salts of dibasic acids.

Fig. 2


Dielectric Constant ε
No. of Carbon Atoms
Sodium salts of monobasic acids.
Potassium salts of monobasic acids.
Calcium salts of monobasic acids.
Barium salts of monobasic acids.

Dielectric Constants.—Fig. 2 gives the curves of the dielectric constants against the number of carbon atoms in the molecule. Dielectric constants also follow the same order as that of the densities, and invariably decrease with the increase in the number of carbon atoms. All the curves are smooth and here also no irregularity is observed in salts containing odd and even number of carbon atoms.

Density-dielectric Constants.—As both the densities and dielectric constants follow the same order and decrease with the number of carbon atoms, it was thought desirable to draw the graphs of densities against the dielectric constants to test the relationship between them. Figure 3 gives such graphs of sodium, potassium, barium and calcium salts. Except in calcium salts which give a curve, the graphs are almost straight lines. Deviations are observed in sodium formate and barium acetate which may be due to these being the first few members. The graphs, straight lines as they are, give a clue to predict approximately the dielectric constant of a salt in series of sodium, potassium and barium salts, if the density is known or *vice versa.*

Molecular Polarisations.—Earlier work on molecular polarisation of inorganic salts by Sathe, Phalanikar and Bhide (this *Journal*, 1945, **22**, 29) shows that in these salts molecular polarisation is not additive. The deviation from the additivity rule has been explained as due to a partial change in the nature of the

Fig. 3

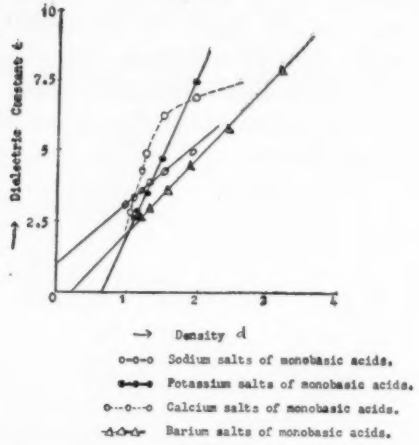
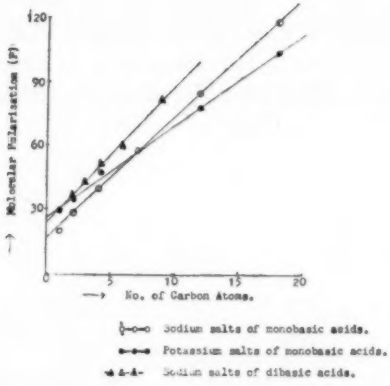


Fig. 4



bond from electrovalent to covalent. In the present work the salts of aliphatic carboxylic acids are under study. In such a series of acids the aliphatic part is mostly non-polar and it may be presumed that the increment in the molecular polarisation with the number of carbon atoms is entirely due to the increment in the molecular volume only. It is seen from Figs. 4 and 5 that in sodium, potassium and barium

Fig. 5

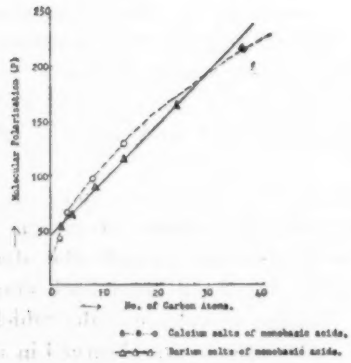
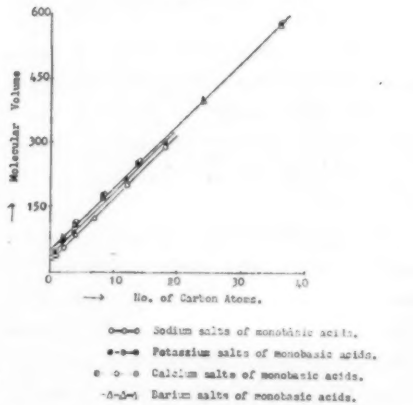


Fig. 6



salts, additivity relationship holds for molecular polarisation if the cation is kept the same; in other words in these salts the cation has no appreciable effect on the polarisation of the organic radical or the anion. In calcium salts the cation seems to have an appreciable effect on the polarisation of the anion.

Though the additivity relationship holds for molecular polarisation in these series of salts, the contribution of polarisation due to each carbon atom, when considered in separate series, does not seem to be identical, as is evident from the following equations (x denoting the number of carbon atoms) :

(1) $P = 5.178x+17.73$ for Na salts of monobasic acids.
(2) $P = 6.296x+24.23$ for „ „ of dibasic acids.
(3) $P = 4.178x+27.91$ for K „ monobasic acids.
(4) $P = 4.712x+46.32$ for Ba „ „ acids.

Thus, the contributions of polarisation due to each carbon atom 5.178, 6.296, 4.178 and 4.712 are different and it be only said that the contribution due to each carbon atom is constant to a particular series of salts of sodium, potassium and barium.

Molecular Volume.—It is well known that in an aliphatic series the molecular volume is an additive property. In this work also it has been found that the molecular volumes of the sodium, potassium, calcium and barium salts of monobasic acids are additive.

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TEMPERATURE DEPENDENCE OF VAPOUR PRESSURE OF SOLUTIONS

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A rigorous derivation of a formula of temperature dependence of vapour pressure of solutions has been made using chemical potentials. For the binary liquid solution it has been deduced that

$$p \cdot \frac{dp}{dT} = \frac{N_1' L_1^D + N_2' L_2^D}{RT^2}$$

where N_1' and N_2' are the molar fractions of the components 1 and 2 in the vapour phase, and L_1^D and L_2^D are the respective heats of evaporation from solution. For solutions of non-volatile solute, the change of vapour pressure with temperature is given by

$$\frac{1}{p} \cdot \frac{dp}{dT} = \frac{L_1^D}{RT^2}$$

Sackur ("Text-book of Thermochemistry and Thermodynamics", 1917, p. 248) and Planck ("Treatise on Thermodynamics", p. 1927, p 204) have mentioned relations for the variation of pressure with temperature for solutions of non-volatile solutes. Guggenheim ("Modern Thermodynamics", 1933, p. 120) has given expressions for the change of partial pressure with temperature. The case of temperature dependence of vapour pressure of saturated solution in contact with the solid solute has also been considered (cf. Glasstone, "Thermodynamics for Chemists", 1940, p. 241). It appears from a survey of literature that a suitable expression connecting the temperature dependence of vapour pressure of solutions with the partial pressures and the molar fractions of the components is lacking. The purpose of the present paper is to derive a suitable relation applicable to various cases.

When a solution having two components, both of which are volatile, is in equilibrium with its vapour, then it has to satisfy the conditions

$$\mu_1 = \mu_1' \text{ and } \mu_2 = \mu_2'$$

where μ_1 and μ_2 are chemical potentials (partial molar free energies) of the components 1 and 2 in the liquid phase, and μ_1' and μ_2' are the corresponding chemical potentials in the vapour phase. If the temperature of the system is slightly altered keeping the two phases in equilibrium by the change of pressure and consequent change in composition, then it follows that

$$d\mu_1 = d\mu_1' \text{ and } d\mu_2 = d\mu_2'.$$

The above changes in chemical potential can be represented as follows by using the well known laws of thermodynamics, assuming that the volume of the solution is very large in comparison with that of the vapour so that the change in liquid composition due to temperature variations is negligible.

$$d\mu_1 = -\overline{S}_1 dT + \overline{V}_1 dp \quad \ldots \quad \ldots \quad (1)$$

$$d\mu_2 = -\overline{S}_2 dT + \overline{V}_2 dp \quad \ldots \quad \ldots \quad (2)$$

$$d\mu_1' = -\bar{S}_1' dT + \bar{V}_1' dp + \left(\frac{d\mu_1'}{dN_1'}\right)_{T,p} dN_1' \quad \ldots \quad (3)$$

$$d\mu_2' = -\bar{S}_2' dT + \bar{V}_2' dp + \left(\frac{d\mu_2'}{dN_2'}\right)_{T,p} dN_2' \quad \ldots \quad (4)$$

In these expressions $\bar{S}$ and $\bar{V}$ indicate partial molar entropy and volume respectively and N indicates molar fraction. Further, 1 or 2 placed next to a symbol refers to component 1 or 2 respectively. If the symbol, is dashed it referst to the vapour phase, otherwise to the liquid phase.

Since $d\mu_1 = d\mu_1'$ and $d\mu_2 = d\mu_2'$, we get equation (5) by equating right-hand side of equation (1) with that of (3), and obtain equation (6) in a similar way from equations (2) and (4).

$$-(\bar{S}_1' - \bar{S}_1)dT + (\bar{V}_1' - \bar{V}_1)dp = -\left(\frac{d\mu_1'}{dN_1'}\right)_{T,p} dN_1' \quad \ldots \quad (5)$$

$$-(\bar{S}_2' - \bar{S}_2)dT + (\bar{V}_2' - \bar{V}_2)dp = -\left(\frac{d\mu_2'}{dN_2'}\right)_{T,p} dN_2' \quad \ldots \quad (6)$$

Now if we assume the vapour phase to be ideal, we have

$$\bar{V}_1' = \frac{RT}{p}; \quad \bar{V}_2' = \frac{RT}{p}$$

(cf. Guggenheim, *loc cit.*). p. 67). Also we can put

$$\bar{S}_1' - \bar{S}_1 = \frac{L_1^D}{T} \text{ and } \bar{S}_2' - \bar{S}_2 = \frac{L_2^D}{T},$$

where L_1^D and L_2^D are the respective latent heats of evaporation from solution.

Neglecting the specific volumes of the components in the liquid phase in comparison wih the respective volumes of their vapour and making p roper substitutions, equations (5) and (6) yield

$$-\frac{L_1^D}{T} \cdot dT + \frac{RT}{p} \cdot dp = -\left(\frac{\delta\mu_1'}{\delta N_1'}\right)_{T,p} dN_1' \quad \ldots \quad (7)$$

$$-\frac{L_2^D}{T} \cdot dT + \frac{RT}{p} \cdot dp = -\left(\frac{\delta\mu_2'}{\delta N_2'}\right)_{T,p} dN_2' \quad \ldots \quad (8)$$

Multiplying equation (7) by N_1' and (8) by N_2' and adding, we have

$$-\frac{N_1'L_1^D + N_2'L_2^D}{RT} \cdot dT + (N_1' + N_2')\frac{RT}{p} \cdot dp = -\left\{ N_1'\left(\frac{\delta\mu_1'}{\delta N_1'}\right)_{T,p} d_1' + N \; ;' \left(\frac{\delta\mu_2' N}{\delta N'}\right) dN_2' \right\} \quad \ldots \quad (9)$$

But by Gibbs-Duhem relation

$$N_1'\left(\frac{\delta\mu_1'}{\delta N_1'}\right) dN_1' + N_2'\left(\frac{\delta\mu_2'}{\delta N_2'}\right) dN_2' = 0$$

and hence equation (9) yields

$$-\frac{N_1'L_1^D + N_2'L_2^D}{T} \cdot dT + (N_1' + N_2') \cdot \frac{RT}{p} dp = 0 \quad (10)$$

giving

$$\frac{1}{p} \cdot \frac{dp}{dT} = \frac{N_1'L_1^D + N_2'L_2^D}{RT^2} \quad \ldots \quad (11)$$

L_1^D may be shown to be equal to $L^\circ - L_D$ from Hess's law, where L° is the heat of evaporation of pure component and L_D is the heat absorbed when 1 g. mol. of the component is added to a large volume of the solution.

For a solution of non-volatile solute (component 2) $N_2'=0$ and $N_1'=1$. Hence for such cases (11) becomes

$$\frac{1}{p} \cdot \frac{dp}{dT} = \frac{L_1^D}{RT^2} \qquad (12)$$

The integration of the above equation, assuming L_1^D not to vary with temperature, yields

$$\ln p = -\frac{L_1^D}{RT} + \text{constant} \qquad \ldots \qquad (13)$$

From equation (13) it is clear that plot of $\log p$ against $1/T$ should be a straight line within a small range of temperature. This explains the straight line plot obtained by Roehl (*J. Amer. Chem. Soc.*, 1936, **58**, 1291)in case of several solutions. We have also obtained similar results in case of several aqueous solutions of electrolytes (this *Journal*, 1951, **28**, 597). If L_1^D does not differ much from the latent heat of vaporisation of the pure solvent, the straight line will be parallel to the corresponding curve for the solvent as has been observed by Roehl (*loc. cit.*). On the other hand, if L_1^D differs much from the latent heat of vaporisation of the pure solvent, this will not be the case. This particularly happens in solutions of hydrated salts (cf. Ewing, *J. Amer. Chem. Soc.*, 1937, **59**, 1293).

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RELATION BETWEEN THE LATTICE ENERGY, MELTING POINT AND BOILING POINT OF SOME CRYSTALLINE SUBSTANCES. PART I. THE ALKALI HALIDES

By Ram Gopal

It is found that the expressions lattice energy (U_o)/melting point (T_m) and (U_o)/boiling point (T_b) are approximately constant for the alkali halides. Slightly higher values for the halides of Li appear to be due to the presence of covalency.

It appears that the potential energy (U_g) of the gaseous state bears an approximate constant ratio to the respective U_o in these systems. Making use of this relationship it has been shown that U_o/T_b should be approximately constant.

Trouton's rule (*Phil. Mag.*, 1884, **18**, 54) and its later improvements by Nernst (*Nachrichten*, 1906), Bingham (*J. Amer. Chem. Soc.*, 1906, **28**, 723), Forcrand (*Compt. rend.*, 1913, **156**, 1439, 1648, 1809), Hildebrand (*J. Amer. Chem. Soc.*, 1915, **37**, 970 ; 1918, **40**, 45 ; *J. Chem. Phys.*, 1939, **7**, 233) and Halford (*J. Chem. Phys.*, 1940, **8**, 496) describe the behaviour of liquids during evaporation. Similar empirical and semi-empirical attempts to study the behaviour of solids at the melting point have been made by Walden (*Z. Elektrochem.*, 1908, **14**, 713), Kordes (*Z. anorg. Chem.*, 1927, **160**, 67) and others. Rigorous mathematical procedures have been adopted by Erying (*J. Chem. Phys.*, 1937, **5**, 396), Lennard-Jones and Devonshire (*Proc. Roy. Soc.*, 1939, **169A**, 317 ; 1939, **170A**, 464) and Rice (*J. Chem. Phys.*, 1939, **7**, 136, 883 ; 1941, **9**, 121 ; 1944, **12**, 1) to study the liquid systems. It appears, however, that these authors have mostly confined themselves either to substances which are liquids at ordinary temperatures or to liquid metals. Substances which melt at higher temperatures to give liquids containing ions appear to have received only very scanty attention.

As the solid is gradually heated from the absolute zero upwards through the melting point into the liquid state, and then finally at the boiling point into vapour, the substances goes on absorbing heat energy which operates against the binding forces of the constituents of the lattice in the crystal, and thus the potential energy (*i. e.* the lattice energy, U_o) of the lattice constituents is reduced with a corresponding increase in their kinetic energy. As the properties of a crystal, such as the lattice energy, the m. p. and the b. p. represent directly or indirectly the magnitude of the ionic forces, and hence its stability (cf. Stillwell, "Crystal Chemistry", 1938, p. 213 ff.), one might expect to discover a possible relationship between the lattice energy, m. p.* and b. p. of the crystalline substances. The present communication is an outcome of such an attempt.

* Relationship between the unit-cell dimensions of crystals and their melting points in the case of halogenobenzenes and methylbenzenes has been investigated by T. Beacall (*Trans. Faraday Soc.*, 1943, **39**, 214 ; 1945, **41**, 472).

The data regarding lattice energy (U_o), m. p. (T_m) and the b. p. (T_b) have been obtained from the Landolt-Börnstein Tables, International Critical Tables, Handbook of Physics and Chemistry (1944), "Electronic Structure and Chemical Binding" (1940) by O. K. Rice, and "Introduction to Physical Chemistry" (1940) by Moelwyn Hughes: these have been utilised for the calculation of various quantities considered in this communication.

TABLE I

Substance.	U_o (k cals./mole).	T_m.	T_b	U_o/T_m.	U_o/T_b.
LiF	240.1	1143	1943	0.2115	0.1236
LiCl	199.2	886	1656	0.2249, 0.12030	0.1203
LiBr	188.2	820	1538	0.2296	0.1224
LiI	174.2	719	1463	0.2423	0.1190
NaF	213.4	1253	1973	0.1703	0.1081
NaCl	183.1	1077	1686	0.1700	0.1086
NaBr	174.6	1028	1663	0.1700	0.1051
NaI	163.9	924	1573	00.1774	0.1042
KF	189.7	1153	1773	0.1645	0.1070
KCl	165.4	1048	1689	.1585	0.0979
KBr	159.3	1003	1653	0.1588	0.0943
KI	150.8	996	1603	0.1515	0.0941
RbF	181.6	1033	1683	0 1758	0.1079
RbCl	160.1	988	1663	0.1620	0.0962
RbBr	153.5	957	1613	0.1604	0.0952
RbI	145.3	913	1573	0.1592	0.0924
CsF	173.7	956	1523	0.1817	0.1140
CsCl	152.2	919	1563	0.1656	0.0974
CsBr	146.3	909	1573	0.1610	0.0931
CsI	139.1	894	1553	0.1556	0.0896

The values of the lattice energy U_o for different substances obtained from the Born-Haber Cycle experimentally and those calculated theoretically agree closely (cf. Moelwyn-Hughes, *loc. cit.*). T_m is given in degree absolute.

Lattice Energy and Melting Point

It appears that except for the lithium salts the values of U_o/T_m are very nearly constant for the different halides of Na, K, Rb and Cs, the extreme values being 0.1515 (KI) and 0.1817(CsF), the average being 0.1615. It appears most probable that the substances which fuse to give liquids containing constituents in a similar state of mutual interaction, give nearly equal values for U_o/T_m. In lithium halides, where covalency is appreciable (cf. Evans, "Crystal Chemistry", pp. 180-82), the values

of U_o/T_m are higher. Due to the presence of covalency there is no uniform distribution of attractive forces, and thus loosening of some parts occurs as compared to others. This causes the substance to melt at a lower temperature than would be the case if a uniform distribution of the lattice forces were present.

Lattice Energy and the Boiling Point

The conclusions arrived at from the study of the ratio U_o/T_m are also supported by the study of the ratio U_o/T_b. The boiling point T_b and the values of U_o/T_b are given in Table I. Here again, except for slightly higher values of U_o/T_b for lithium halides, the values for the halides of other alkali metals are very nearly constant, the extreme values being 0.08958(CsI) and 0.1140(CsF) and average being 0.1020. The higher values of U_o/T_b for lithium halides are perhaps due to covalency, as explained previously.

The study of the ratio U_o/T_b becomes all the more interesting if we take into consideration the potential energy of the gaseous state (U_g) and as will be clear from Table II, it appears to be an approximate constant fraction of the respective U_o *i. e.* U_o/U_g is approximately constant for similar substances. This is clear from Table II.

TABLE II

(The values of U_o have been taken from Table I)

Substance.	U_g (kcal./mole).*	U_o/U_g.	Substance.	U_g (kcal./mole).*	U_o/U_g.
LiF	192	1.240	KF	134	1.403
LiCl	140	1.393	KCl	111	1.469
LiBr	130	1.423	KBr	106	1.481
LiI	117	1.462	KI	99	1.505
NaF	160	1.331	RbF	125	1.440
NaCl	126	1.396	RbCl	106	1.490
NaBr	119	1.445	RbBr	101	1.490
NaI	108	1·448	RbI	95	1.505

* See Moelwyn-Hughes, *loc. cit.*

The consequences of this relationship must be far reaching. It implies that boiling in similar substances (*i. e.* those in which U_o is similarly distributed in the lattice) appears to occur at such a temperature at which U_g bears approximately the same ratio to U_o of the substance in question. This will result in an approximate constancy of U_o/T_b. This can be shown as follows :

$$U_o/U_g = \frac{U_o - L_t - L_e - H}{U_o} \quad \ldots \quad (1)$$

$$\text{or a constant } C = 1 - \frac{L_t}{U_o} - \frac{L_e}{U_o} - \frac{H}{U_o} \quad \ldots \quad (1)$$

where H = heat absorbed in raising T from $0°K$ to T_b ; L = latent heat of fusion ; L_e = latent heat of evaporation.

It can be reasonably assumed* that L_f and L_e, under similar conditions, would be roughly proportional to U_o in similar substances. Hence (1) gives

$$C = K - \frac{H}{U_o} \qquad \ldots \qquad (2)$$

Again roughly $C_p T_b \approx C_v T_b \approx 3nRT_b \approx 6nT_b$, where n is the number of atoms in the molecule.

Hence (2) gives

$$K - C \approx 6nT_b/U_o - B$$

or $$U_o/T_b \approx \frac{6n}{K-C} \approx \frac{6n}{B} - K_1$$

Similarly U_o/T_m can be shown to be approximately constant for similar substances.

Thus, one is lead to conclude that :

(*i*) Substances in which the lattice energy is similarly distributed among the various constituents of the lattice, give approximately a constant value for U_o/T_m and U_o/T_b. In such cases it appears from available evidence that the potential energy of the gaseous state bears an approximate constant ratio to the lattice energy of the crystal.

(*ii*) If a part of the lattice energy is bound in covalency, e. g. in lithium halides, the ratios U_o/T_m and U_o/T_b have higher values than those for purely electrovalent systems. In such cases the values of T_m and T_b would be, in general, comparatively low.

(*iii*) The boiling points and, to a lesser extent, the melting points for similar substances may be considered as the corresponding temperatures even for alkali halides which are, at ordinary temperatures, crystalline solids.

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* It is almost impossible to support this assumption by experimental evidence as the values of L_f and L_e are not known in many cases. However, as both L_f and L_e would be small as compared to U_o, L_f/U_o and L_e/U_o will be neglible as compared to unity.

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SEARCH FOR NEW INSECTICIDES. PART V

By A. B. Sen and S. S. Parmar

Several *ortho*-chlorobenzyl and allyl ethers of *ortho*-acyl-*p*-bromophenol have been prepared with a view to testing their insecticidal activity.

The benzylaryl and allylaryl ethers of halophenols may be expected to be good contact insecticides, in view of the fact that they contain a neurotoxic haloaryl group and an ether linkage having lipophilic properties (T. C. Chen and Sumerford. *J. Amer. Chem. Soc.*, 1951, **73**, 4694). The introduction of the ketonic group, which would possibly increase their lipoid solubility, may further enhance their insecticidal activity. Attempts have now been made to combine these insecticidally active groups in order to obtain additional and possibly improved insecticides. For this purpose two series of ethers, viz., *ortho*-chlorobenzylaryl and allylaryl ethers of *ortho*-acyl-*p*-bromophenols were prepared having one halogen atom in the benzene nucleus as *para* substituent. The *ortho*-hydroxyketones were prepared in the usual manner by the Fries rearrangement of the appropriate esters of *p*-bromophenol. These ketones were converted into *o*-chlorobenzyl and allyl ethers by refluxing a mixture of the appropriate *o*-hydroxyketone with an equivalent amount of *o*-chlorobenzyl chloride or allyl bromide and freshly fused potassium carbonate in acetone on a water-bath for 8 hours. The ketonic ethers, thus obtained, were characterised through their 2:4-dinitrophenylhydrazones which were recrystallised from hot glacial acetic acid.

Experimental

The esters of *p*-bromophenol, viz., acetate, propionate, butyrate, valerate, caproate and heptoate were prepared in the usual manner (*J. Amer. Chem. Soc.*, 1933, **55**, 4657). The ester of heptylic acid was analysed. (Found : C, 54.31 ; H, 5.67. $C_{13}H_{17}O_2Br$ requires C, 54.74 ; H, 5.97 per cent).

Fries Rearrangement of the Esters.—The rearrangement of the above esters was carried out in the usual manner. The *o*-hydroxyketone obtained from the ester of heptylic acid was analysied. (Found : C, 54.52 ; H, 5.57. $C_{13}H_{17}O_2Br$ requires C, 54.74 ; H, 5.57 per cent). This 5-bromo-2-hydroxyheptophenone was converted into its 2 : 4-dinitrophenylhydrazone which was crystallised from hot glacial acetic acid, m. p. 189°. (Found : N, 11.68. $C_{19}H_{21}O_5N_4Br$ requires N, 12.04 per cent).

Preparation of o-Chlorobenzylaryl and Allylaryl Ethers.—A mixture of *o*-hydroxyketone (0.1 *M*), an equivalent quantity of *o*-chlorobenzyl chloride or allyl bromide, freshly fused potassium carbonate and acetone (100 c. c.) was refluxed on the water-bath for 8 hours. A heavy precipitate of potassium halide began to form soon after the refluxing was started. After cooling, water was added and the mixture was taken up in ether. The ether solution was washed with 10% NaOH solution. The ethereal layer was further washed with water and dried over freshly fused potassium carbonate, the ether removed and the residual oil was distilled under reduced pressure. The *o*-chlorobenzylaryl and allylaryl ethers were thus obtained in yields ranging from 54.5 to 83.5% (Tables I and II). These ethers were characterised through their 2 : 4-dinitrophenylhydrazones.

TABLE I

o-Hydroxy-ketones.	*o*-Chlorobenzyl ether B.P.	Yield.	Mol. formula.	% Carbon. Found.	Calc.	% Hydrogen. Found.	Calc.	2 : 4-Dinitrophenylhydrazone Mol. formula.	M.p.	% Nitrogen. Found.	Calc
R-acetophenone	119°/6 mm.	54.5%	$C_{15}H_{12}O_2ClBr$	52.87	53.02	3.13	3.53	$C_{21}H_{16}O_5N_4ClBr$	252°	10.35	10.78
R-propiophenone	107°/5	77.7	$C_{16}H_{14}O_2ClBr$	53.96	54.32	3.67	3.94	$C_{22}H_{18}O_5N_4ClBr$	173°	10.03	10.50
R-butyrophenone	152°/6	79.3	$C_{17}H_{16}O_2ClBr$	55.08	55.51	3.89	4.35	$C_{23}H_{20}O_5N_4ClBr$	184°	9.78	10.23
R-valerophenone	157°/6	80.8	$C_{18}H_{18}O_2ClBr$	56.13	56.62	4.31	4.72	$C_{24}H_{22}O_5N_4ClBr$	195°	9.61	9.97
R-caprophenone	209°/6	71.3	$C_{19}H_{20}O_2ClBr$	57.22	57.65	4.76	5.06	$C_{25}H_{24}O_5N_4ClBr$	163°	9.25	9.73
R-heptophenone	138°/5	83.5	$C_{20}H_{22}O_2ClBr$	58.39	58.61	4.92	5.37	$C_{26}H_{26}O_5N_4ClBr$	129°	9.01	9.50

R = 5-bromo-2-hydroxy.

TABLE II

o-Hydroxy-ketones.	Allyl erher M.P. or B.P.	Yield.	Mol. formula.	% Carbon Found.	Calc.	% Hydrogen Found.	Calc.	2 : 4-Dinitrophenylhydrazone Mol. formula.	M.p.	% Nitrogen Found.	Calc.
R-acetophenone	58°	62.4%	$C_{11}H_{11}O_2Br$	51.35	51.76	4.02	4.31	$C_{17}H_{15}O_5N_4Br$	147°	12.38	12.87
R-propiophenone	64°	59.6	$C_{12}H_{13}O_2Br$	53.18	53.53	4.35	4.83	$C_{18}H_{17}O_5N_4Br$	132°	12.06	12.47
R-butyrophenone	69°	58.4	$C_{13}H_{15}O_2Br$	54.89	55.12	4.92	5.30	$C_{19}H_{19}O_5N_4Br$	148°	11.92	12.10
R-valerophenone	210°/6 mm.	61.2	$C_{14}H_{17}O_2Br$	56.14	56.57	5.57	5.72	$C_{20}H_{21}O_5N_4Br$	188°	11.36	11.74
R-caprophenone	230°/6	62.7	$C_{15}H_{19}O_2Br$	57.52	57.88	5.91	6.11	$C_{21}H_{23}O_5N_4Br$	146°	10.98	11.41
R-heptophenone	239°/6	79.0	$C_{16}H_{21}O_2Br$	58.76	59.08	6.03	6.46	$C_{22}H_{25}O_5N_4Br$	152°	10.76	11.09

R = 5-bromo-2-hydroxy.

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STUDIES ON THE FRIES REARRANGEMENT. PART IX

By A. B. Sen and S. S. Parmar

The Fries rearrangement of five esters of carvacrol has been studied. The *o*-hydroxyketones obtained were further converted into alkylcarvacrols by the Clemmensen reduction.

The Fries rearrangement of carvacryl acetate has been studied (Eykmann, *Chem. Weekbld.*, 190 1, 453). We have now extended it to five new esters of carvacrol, viz., propionate, butyrate, valerate, heptoate and caprylate, which were prepared by the action of the appropriate acid chlorides on carvacrol. The rearrangement was carried out at 120° (without a solvent) using 1.3 to 1.5 moles of anhydrous aluminium chloride. In all the cases studied, only *o*-hydroxyketones were obtained. The mother-liquor after the removal of the *o*-hydroxyketone was worked up for the *para* isomer, which was found absent. The hydroxyketones obtained conformed to Pyman's test (*J. Chem. Soc.*, 1930, 280) for *o*-hydroxyketones and were characterised through their 2 : 4-dinitrophenylhydrazones. These ketones were converted into their corresponding alkylphenols by the Clemmensen reduction through the use of amalgamated zinc and hydrochloric acid.

Experimental

Esters of Carvacrol.—The esters of carvacrol were prepared as described in the earlier parts of this series in yields ranging from 82.6 to 97.9%. They are summarised in Table I.

Table I

Carvacryl esters.	Ester B P.	Yield.	Mol. formula.	%Carbon. Found.	Calc.	% Hydrogen. Found.	Calc.
1. Propionate	121°/3 mm.	89.6%	$C_{13}H_{18}O_2$	75 31	75.71	8.26	8.74
2. Butyrate	133°/3	92.1	$C_{14}H_{20}O_2$	75.94	76.37	8.91	9.09
3. Valerate	137°/3	88.1	$C_{15}H_{22}O_2$	76.37	76.93	8.96	9.40
4. Heptoate	158°/3	97.9	$C_{17}H_{26}O_2$	77.61	77.85	9.46	9.92
5. Caprylate	178°/3	82.6	$C_{18}H_{28}O_2$	77.83	78.27	9.87	10.15

The Fries rearrangement of the Esters.—The Fries rearrangement of the esters was carried out at 120° (without solvent) as described in the earlier parts of this series. The *o*-hydroxyketones obtained are summarised in Table II.

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TABLE II

	Carvacryl esrers.	Ketone formed.	B.P.	Yield.	Ketone. Found % C.	Ketone. Found % H.	Ketone. Calc % C.	Ketone. Calc % H.	M.p.	2 : 4-Dinitrophenylhydrazone Molecular formula.	% Nitrogen. Found.	% Nitrogen. Calc.
1.	Propionate	*R-ethyl-K**	164°/6. mm.	71.4%	75.26	8.29	75.71	8.74	187°	$C_{19}H_{22}O_5N_4$	14 08	14.51
2.	Butyrate	R-*n*-propyl-K	142°/3	70.0	75.98	8.71	76.37	9.09	167°	$C_{20}H_{24}O_5N_4$	13.62	14.00
3.	Valerate	R-*n*-butyryl-K	154°/3	65.8	76.56	9.01	76.93	9.40	136°	$C_{21}H_{26}O_5N_4$	13 07	13.53
4.	Heptoate	R-*n*-hexyl-K	176°/3	73.3	77.43	9.56	77.85	9.92	122°	$C_{23}H_{30}O_5N_4$	12.28	12 67
5.	Caprylate	R-*n*-heptyl-K	255°/10	60.0	78.0	9.83	78.27	10.15	127°	$C_{24}H_{32}O_5N_4$	11.92	12.28

* R = carvacryl.

** K = ketone.

Clemmensen Reduction of the o-*Hydroxyketones.*—A mixture of zinc (20 g.), mercuric chloride (2 g.), concentrated hydrochloric acid (20 c. c.) and 10 c. c. of water was shaken for 10 minutes. The aqueous solution was decanted and the zinc washed with water. The amalgamated zinc was then covered with 30 c. c. of alcohol. Now to this 5 g. of *o*-hydroxyketone and 10 c. c. of concentrated hydrochloric acid were added. The mixture was refluxed on the water-bath till a drop of the liquid gave no colour with aqueous ferric chloride solution. The completion of the reaction took nearly 8-10 hours. During this period 2 c. c. portion of concentrated hydrochloric acid was added after each hour of heating. Alcohol was then distilled off and the mixture was cooled and extracted with ether. The ethereal layer was successively washed with 2% sodium carbonate solution and water. The ethereal extract was then dried over anhydrous calcium chloride and the ether removed by distillation. The residual oil was then distilled under reduced pressure, yield 50 to 56%. The alkylcarvacrols, thus obtained, are summarised in Table III. (No crystalline derivative of these alkylcarvacrols could be prepared).

TABLE III

	Ketone*	Alkyl carvacrol.	B.P.	Yield.	Molecular formula.	Found		Calc.	
						% C.	% H.	% C.	% H.
1.	R-ethyl-K	*n*-Propyl	142°/6mm.	50%	$C_{11}H_{20}O$	79.78	10.06	81.24	10.42
2.	R-*n*-propyl-K	*n*-Butyl	231°/9	50	$C_{14}H_{22}O$	81.09	10.21	81.55	10.68
3.	R-*n*-butyl-K	*n*-Amyl	160°/4	52	$C_{15}H_{24}O$	81.36	10.48	81.82	10.91
4.	R-*n*-hexyl-K	*n*-Heptyl	205°/10	56	$C_{17}H_{28}O$	81.87	10.98	82.26	11.29
5.	R-*n*-heptyl-K	*n*-Octyl	168°/4	56	$C_{18}H_{30}O$	82.01	11.12	82.44	11.45

* R = Caryacryl.
K = Ketone.

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LIBERATION OF IODINE BY "FORMAMIDINE DISULPHIDE" SALTS. CONSTITUTION OF 'FORMAMIDINE DISULPHIDE SALTS'

By R. H. Sahasrabudhey

Influence of dilution, concentration of KI, addition of acids and thiocarbamide, and the dielectric constant of the medium on the change of thiol⇄disulphide have been investigated by titrating the amount of iodine set free and the acid formed.

Reynolds and Werner (*J. Chem. Soc.*, 1903, **83**, 1) found that within certain limits thiocarbamide, like mercaptans, could be titrated directly with iodine (cf. Klason and Carlson, *Ber.*, 1906, **39**, 738; *J. Amer. Chem. Soc.*, 1921, **43**, 119; Sampey and Reid., *ibid.*, 1932, **54**, 3404), Thus,

$$2\ H_2N.C(SH):NH + 2\ I \xrightarrow{-2H} \left[H_2N.C(S.S).C.NH_2 \text{ (HN, NH)}\right],\ 2\ HI$$

(I)

"Formamidine disulphide" salt.

The reversible nature of the above reaction, however, was recognised first by Werner (*J. Chem. Soc.*, 1912, **101**, 2166). According to him, the liberation of iodine, under certain conditions from alkali iodide, by "formamidine disulphide" salts (since the free base is not known) is due to the reverse reaction of the above change, the acid (or anion) forming salt with the base having no primary function in this regard. Since (*i*) reversibility in the true physico-chemical sense, as distinct from more or less ease of oxidation and reduction, in the process Thiol⇄Disulphide, generally, is doubtful and a subject of controversy (*Ann. Rev. Biochem.*, 1949, **18**, 27, 28; Michaelis, "Physical Methods of Organic Chemistry", Vol. II. Ed. by Weissberger, 1946, p. 1109; Preisler and Berger, *J. Amer. Chem. Soc.*, 1947, **69**, 322), and (*ii*) results throwing doubt on the disulphide structure of "formamidine disulphide" have been already reported (this *Journal*, 1951, **28**, 119, 309, 341), a re-examination of the above system appeared warranted. Experiments were therefore undertaken to investigate the influence of dilution, potassium iodide concentration, addition of acids and thiocarbamide, and of dielectric constant of the medium, on the above change; in each case the quantity of iodine set free and acid formed were measured. For comparison similar observations were taken with "tetramethylformamidine disulphide" hydrobromide (Lecher, *Annalen*, 1925, **445**, 36, 51; Sahasrabudhey, *loc. cit.*) and those with respect to dilution and potassium iodide concentration are reported. The results are presented in Tables I to VIII and Fig. 1.

Experimental

Influence of Dilution.—"Formamidine disulphide" hydrobromide (1.4 g.) was dissolved to give 20 c. c. solution and 2 c. c. of this were diluted with varying quantities of water and treated with a fixed quantity (2 c. c.) of 20% potassium

iodide solution. Iodine was at once liberated, which was determined titrimetrically with a *N*/10 thiosulphate solution using starch as an indicator. This was followed by an estimation of the acidity of the solution with *N*/10-sodium hydroxide. The results are summarised in Table I.

TABLE I

The hydrobromide soln. taken = 2 c. c.

Expt. No.	Dilution.	KI.	*N*/10- Thio.	*N*/10-Alkali.	Total thio + alkali.
1	—	—	—	9.0 c.c.	9.0 c.c.
2	—	(Excess of solid KI)	8.5 c.c.	0.5	9.0
3	—	2 c.c.	4.1	4.9	9.0
4	10 c.c.	,,	3.95	5.0	8.95
5	25	,,	3.7	5.3	9.0
6	100	,,	2.8	5.85	8.65
7	200	,,	1.0	7.95	8.95
8	400	,,	0.25	8.65	8.96

Influence of Potassium Iodide Concentration.—"Formamidine disulphide" hydrobromide (1.56 g.) was dissolved to give 20 c. c. solution and to a fixed volume of it varying quantities of a strong potassium iodide solution (50%) were added and the bulk of the mixture made up to a fixed volume. Iodine and acid liberated were determined. The results are presented in Table II.

TABLE II

Hydrobromide soln. = 2 c. c. Bulk of the mix. = 11.0 c. c.

Expt. No.	KI.	H_2O added.	Thio.	*N*/10- Alkali	Alkali + thio.
1	5.0 c.c.	5.0 c.c.	4.50 c.c.	5.4 c.c.	9.90 c.c.
2	2.5	7.5	3.85	6.0	9.85
3	1.25	8.75	3.55	6.3	9.85
4	0.60	9.4	3.20	6.6	9.80
5	0.30	9.7	2.65	7.2	9.85

Influence of the added Acid.—"Formamidine disulphide" hydrobromide (0.79 g.) was dissolved to give 20 c. c. solution, 2 c. c. of which were treated with varying volumes of 5*N* sulphuric acid and a fixed quantity of potassium iodide. In each case the final bulk of the mixture was made up to 20 c. c. with water and the liberated iodine estimated. The results are presented in Table III.

TABLE III

Hydrobromide soln.—2.0 c. c. Vol. of the mixture—20 c. c. 50% KI—5 c. c.

Expt. No. ...	1	2	3	4	5	6
$5N$-H_2SO_4 added (c.c.) ...	1.0	3.0	5.0	7.0	10.0	12.0
N/10-Thio (c.c.) ...	3.0	3.1	3.3	3.35	3.5	3.7

Influence of addition of Thiocarbamide.—The hydrobromide (0.62 g) was dissolved to give 20 c. c. solution. The thiocarbamide solution contained 1.57 g. in 50 c. c. The results are summarised in Table IV.

TABLE IV

Hydrobromide soln.—2.0 c. c. Vol. of the mixture—20 c. c.

Expt. No.	Thiocarbamide.	50% KI.	N/10- Thio.	N/10-alkali.	Thio + alkali.*
1	2.0 c.c.	5.0 c.c.	2.7 c.c.	1.1 c.c.	3.8 c.c.
2	5.0	,,	2.3	1.6	3.9
3	7.0	,,	2.2	1.6	3.8
4	10.0	,,	2.1	1.8	3.9
5	12.0	,,	1.9	1.9	3.8

Influence of addition of Hydriodic Acid.—The hydrobromide (1.5 g.) was dissolved to give 20 c. c. solution. Experiments were carried out along the same lines as in Table II, a strong solution of hydriodic acid being used instead of potassium iodide. The results are presented in Table V.

TABLE V

Hydrobromide soln.—2.0 c. c.

Expt. No.	*HI added.	Water added.	N/10- Thio.	N/10- Alkali.	Thio + alkali.
1	—	—	—	9.6 c.c.	9.6 c.c.
2	(Solid KI)	—	9.4 c.c.	0.0	9.4
3	*1.0 c.c.	1.0	4.3	**20.65 (5.0)***	9.3
4	,,	10.0	2.6	22.50 (6.85)	9.45
5	2.0	—	5.0	35.60 (4.30)	9.30
6	4.0	—	6.0	65.40 (2.80)	8.8

* 1 c. c. of HI = 0.1987 g. iodine = 0.26 g. KI = 1.5.65 c. c. N/10-alkali.

** These figures represent the direct titre value.

*** These figures (bracketed) represent the quantity of alkali required for the acid formed from the hydrobromide and have been obtained by subtracting the corresponding HI equivalent (calculated from column 2) from the titre value directly obtained (column 5).

Similar experiments with respect to the influence of dilution and potassium iodide concentration were carried out with the hydrobromide of tetramethylformamidine disulphide (Sahasrabudhey, *loc. cit.*). The results are presented in Tables VI and VII which are self explanatory (cf. Tables I and II).

Tetramethylformamidine disulphide hydrobromide (0.955 g.) was dissolved to give 50 c. c. solution.*

TABLE VI

Influence of dilution.

Hydrobromide soln. = 5.0 c. c.

Expt. No.	KI (20%).	Dilution.	*N*/10- Thio.	*N*/10- Alkali.	Thio + alkali.
1	5.0 c c.	25 c.c.	3.0 c.c.	1 3 c c.	4.3 c.c,
2	,,	50	2.7	1.7	4.4
3	,,	100	2.3	2.05	4.35
4	,,	200	1.6	2.8	4.4
5	,,	400	0.8	3.7	4.5
6	,,	—	4.1	0.3	4.4
7	,,	—	—	4.5	4.5

Influence of Potassium Iodide Concentration.—The tetramethylformamidine disulphide hydrobromide (1.91g) was dissolved to give 50 c. c. solution, 5.0 c.c. of which were used in the experiments in Table VII.

TABLE VII

Vol. of the mixture = 25 c. c.

Expt. No.	KI (20%).	Water added.	*N*/10-Thio.	*N*/10- Alkali.	Alkali + thio.
1	10.0 c.c.	10.0 c.c.	5.9	2,7 c.c.	8.6 c c.
2	5.0	15.0	5.7	2.9	8.6
3	2.5	17 5	5.5	3.1	8.6
4	1.25	18.75	4.95	3.7	8.65
5	0.62	19.4	3.5	5.2	8.7
6	0.31	19.7	2.0	6 9	8.9
7	—	25 0	—	9.0	9.0

*Influence of the Dielectric Constant of the Medium.***—Formamidine disulphide hydriodide (2.03 g., prepared according to Werner's procedure, *loc. cit.*) was dissolved to

* It is not possible to carry out these experiments with about *M*/2 solutions as in the case of "formamidine disulphide" hydrobromide (vide Table I). Approximately *M*/10 solution was therefore used.

** cf. Werner, *J, loc. cit.*

give 20 c. c. solution, 1 c. c. of which was added to a fixed weight of the solvent (alcohol-water mixtures so prepared as to give a wide range of dielectric constants), and the iodine set free estimated colorimetrically as well as titrimetrically with thiosulphate. The results are summarised in Table VIII (Fig. 1).

TABLE VIII

Wt. of the mixture = 20 g.

Expt. No.	% Absolute alcohol in mix. by wt.	D^* at 40°.	Bulk of the mixture.	Iodine set free in terms of $N/10$ thio.	Iodine colorimetrically determined. $N/10$-I_2 (in 20 c.c. bulk).
1	8	70	20.4 c.c.	<0.05 c.c.	Imperceptible
2	16	66	20.8	0.05	Do
3	24	60	21.2	0.10	<0.05 c.c.
4	32	55.5	21.6	0.20	0.05
5	40	51	22.0	0.40	0.10
6	50	45	22.5	0.60	0.15
7	60	39	23.0	0.70	0.25
8	75	32	23.8	0.80	0.40
9	85	27.5	24.2	1.00	0.70
10	100	22.5	25.0	1.80	0.90

* Dielectric constant data as per Landoldt & Börnstein & others, Physikalische-Chemische Table III, p. 1969 by J. Wyman ji.

DISCUSSION

From the results in Table I to VIII it is evident that the reaction

$$2\ CSN_2H_4 + I_2 \rightleftharpoons 2(CSN_2H_4) - I$$

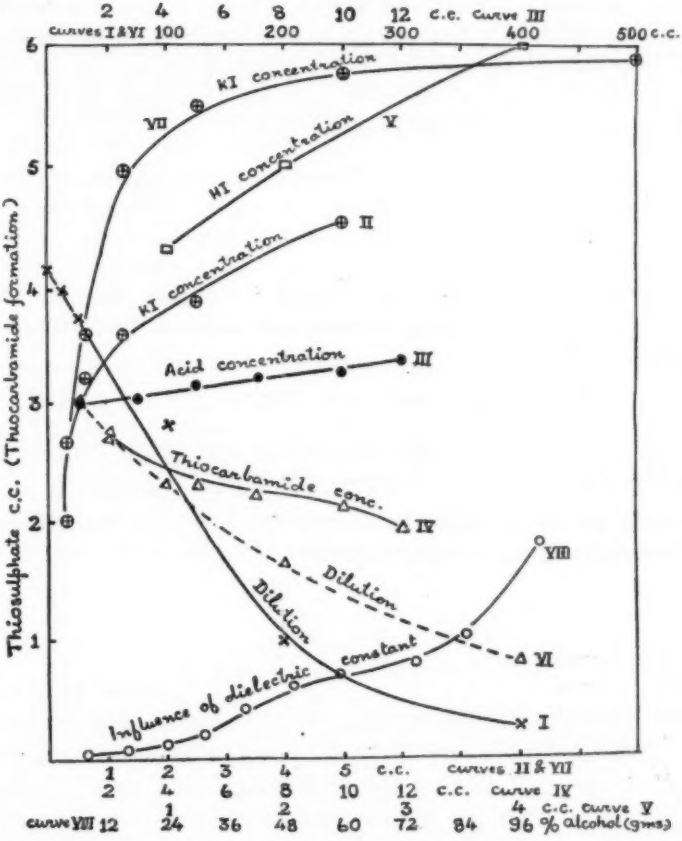
or

$$\left[\begin{matrix} H_2N.C.S.S.C.NH_2 \\ \| \quad\quad \| \\ HN \quad\quad NH \end{matrix}\right], 2\ HI$$

is a truly reversible system, which shows mobility comparable with an ionic process and is influenced, in addition to the concentration of the reactants and resultants, by dilution and the dielectric constant of the medium. Further, since (*i*) the quantity of iodine set free by the reverse change and the acid formed, presumably by the decomposition and/or "hydrolysis" of the "salt" show very definite interdependence, their sum total being always constant, (*ii*) added external acid favours iodine liberation, and (*iii*) this last is also profoundly influenced by the dielectric constant of the medium, *i. e.* in general, factors which would hinder or suppress

dissociation or hydrolysis of the "salt" favour iodine liberation, the conclusion that 'anion" of the "salt" partakes in this change is patent. In short, the iodine liberating capacity is possessed by the "salt" molecule as a whole (unhydrolysed and undissociated) and is not due to the base only, as suggested earlier (Werner, *loc. cit.*). If Werner's mechanism, namely, decomposition of disulphide link (cf. Fromm, *Annalen*, 1906, **348** 144) as a prerequisite of the above reverse change be assumed, the following difficulties arise : (*i*) "anion" of the "formamidine disulphide salt" will

Fig. 1



not partake in such a process, (*ii*) the process will constitute essentially a cleavage of the covalent S-S link which from the known facts about this bond cannot be influenced by ionic processes as has been observed in the present case, and (*iii*) though iodine would be liberated by the neutral free thyil radicals (Lecher, *Ber.*, 1915, **48**, 524 ; 1920, **53**, 577 ; Schonberg, *Trans. Faraday Soc.*, 1934, **30**, 17), if they are formed, their formation is known only in indifferent solvents and on impartation of thermal energy, both of these factors being inoperative in this case.

Another noteworthy feature of the oxidation of thiocarbamide is that the change : thiocarbamide $\longrightarrow$ oxidation product, is known to be reversible only in presence of iodine and the ion I^-, a fact which cannot be explained on the disulphide view of the constitution of the latter. In other reactions where iodine is known to be liberated (by oxidation of HI) by say, the N-haloamides, the conditions applied are vastly different (Whitley *et al.*, *J. Chem. Soc.*, 1921, **119**, 559), and then the process is not reversible.

On the above considerations it is concluded therefore, that the reversibility of the present process (Preisler and Berger, *loc. cit.*) is not due to the reversible disruption of the disulphide link but arises as a result of certain special properties of the link between electron deficient (positive) molecule ion of thiocarbamide formed by the loss of an electron by oxidation (Weitz, *Ber.*, 1926, **59**, 2307 ; Sahasrabudhey, *loc. cit.*, pp. 119, 309) and negative I^-.

$$\left[\begin{matrix} H_2N.C.NH_2 \\ \| \\ S \end{matrix}\right]^+ I^- \longleftrightarrow CSN_2H_4 + I$$

(II)

which combination (II) is bound to be formed (from any "salt" of the base) to a greater or less extent in presence of iodine ions in an ionising medium by a simple exchange process ; thus :

$$(CSN_2N_4)X + HI \text{ or } MI \longrightarrow (CSN_2H_4)I + HX \text{ or } MX.$$

What can the be possible mode of attachment of iodine to the thiocarbamide residue envisaged above is being discussed separately.

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REACTIONS WITH DRY ALKALINE EARTH HYDROXIDES. PART IV. A NEW METHOD FOR THE PREPARATION OF ANILINE

By J. Datta

Nitrobenzene has been reduced to aniline to the extent 54.0% by leading its vapour over a mixture of sulphur and calcium hydroxide containing 20% of sulphur and heated to a temperatue of about 200°.

Several procedures have been suggested for the reduction of liquid nitrobenzene. In the vapour phase, however, the work seems to have been tried only through the agency of gaseous hydrogen, activated by the presence of catalysts (Gladstone and Tribe, *Chem. News*, 1878, **37**, 68; Yosikawa and Yamanuka, *Bull. Inst. Phys. Chem. Res. Japan*, 1925, **14**, 406; Paul and Roth, *Ber.*, 1938, **41**, 2282). According to Griffith and Brown (*J. Phys. Chem.*, 1937, **41**, 477) the yield of aniline can be raised as high as 97% using CoS as the catalyst and a temperature of about 300°. From the work of Sabatier and Sanderenes (*Compt. rend.*, 1902, **135**, 226), however, it appears that the yield of aniline in such processes comes best in the neighbourhood of 200°, an elevation to 300° favouring the formation of ammonia etc.

It has been observed in the earlier studies (this *Journal*, 1952, **29**, 751) that heated mixtures of lime and carbon or lime and sulphur can reduce a nitrate to ammonia. The fate of organic nitro compounds under similar treatment naturally constitutes a matter of interesting study. The object in the present piece of work was to utilise the above mentioned mixtures for the vapour phase reduction of a volatile nitro compound, nitrobenzene being primarily chosen because of the industrial importance associated with aniline, its final reduction product.

Experimental

Nitrobenzene used in this work was one of 'Analar' quality. Other reagents were the same as used in earlier works (this *Journal*, 1952, **29**, 101, 394).

Qualitative tests were conducted by taking 2 c.c. of nitrobenzene in test tubes in each of the experiments and covering the same with respective lime-sulphur mixture in the proportions as shown in Table I. The charge was compressed, provided with a central hole (1 mm.), closed with a delivery tube dipping under dilute HCl, and arranged horizontally as in other experiments described earlier (this *Journal*, 1952, **29**, 394, 751). Heat was first applied to the upper region of the charge with the help of a small flame till a bubble or two of H_2S began to appear. It was then transferred lower to vaporise the nitrobenzene. The starting of the reaction was noticed by the evolution of a rapid stream of H_2S gas and the appearance of a distillation product, either solid or liquid or both in the long delivery tube.

The supply of heat at this stage was controlled by lowering the flame and playing it rapidly, so that the distillation continued at a regular though slow pace, but the evolution of H_2S was reduced to a minimum. It was noticed that with the increase in the supply of heat, volume of the gas evolution and the amount of unchanged nitrobenzene distilled increased. On the other hand, with controlled heating, the distilled liquid dissolved completely in the acid and the gas evolution was totally stopped. As a precautionary measure the individual experiments were carried out for not less than 2 hours. At the close of the experiments, the solid product deposited inside the delivery tube was washed down with alcohol and filtered free of sulphur. The alcoholic solution, on evaporation left varying amounts of a residue which in some cases was in traces or absent. The amount of nitrobenzene distilled out also varied from appreciable to traces or nil. Aniline was detected by basifying the (filtered and boiled) acidic collection in the receiver with an excess of concentrated NaOH solution. In case of amine in trace, it had to be detected by the usual confirmatory tests. Ammonia was found by the intensity of its tests to occur in varying extents in different experiments. Results of the above set of experiments conducted with mixtures of diminishing sulphur concentrations are shown in Table I, where as usual 'p' indicates presence, 'tr', trace formations and 'n', absence of the products referred against. The residue of the reaction was found to contain sulphide, sulphite and sulphate of calcium

TABLE I

Expt. No.	Lime.	Sulphur.	S : $Ca(OH)_2$.	Products			
				Solid.	$PhNO_2$.	$PhNH_2$.	NH_3.
a	22 g.	11 g.	1 : 2	p	p	tr	tr
b	24	8	1 : 3	p	p	tr	tr
c	24	6	1 : 4	tr	tr	p	p
d	25	5	1 : 5	n	n	p	p
e	30	5	1 : 6	n	n	p	p

Identical experiments with calcium hydroxide-carbon mixtures revealed that nitrobenzene distilled out entirely unchanged irrespective of the concentration of carbon.

Quantitative estimation of the aniline, formed by the reduction of nitrobenzene by the above process, was conducted in the same way as described above. The receivers in these cases contained pure water. At the end of the experiment, the heavy liquid, found settled at the bottom of the aqueous layer, was measured out by means of a graduated pipette, treated with a warm solution of HCl (conc., 3 c. c., 15%), and the undissolved nitrobenzene remeasured. From the readings obtained the volumes of the reacted nitrobenzene and the corresponding

aniline formed were found out. Results of the experiments with 5 c. c. of nitrobenzene in each case are shown in Table II.

TABLE II

Expt. No.	$Ca(OH)_2$.	Sulphur.	Aniline found.	% Transformation.
a	32 g.	4 g.	2.04 g.	45.0
b	35	5	2.24	49.3
c	36	6	2.34	51.5
d	35	7	2.45	54.0

The optimum temperature at which the reduction of nitrobenzene to aniline took plane was determined as in the manner described in Part I (this *Journal*, 1952, **29**, 101). Nitrobenzene (2 c. c.) was taken in each case and covered with 30 g. of the mixture of lime and sulphur having the same composition as in Table II. The compressed charge, after being fitted with a thermometer at the centre of the mass and a delivery tube, was placed horizontally on a stand. A preliminary heating was given with the help of a small flame to raise the temperature of the mass to about 100°. The flame was then localised mainly below the region containing the bulb of the thermometer, but occasionally removed to the bottom to ensure the distillation of nitrobenzene. As soon as the droplets of aniline, emulsified with water, were seen to appear in the receiver, the flame was lowered at least six inches below the tube, so that only a current of warm air grazed its surface serving as an insulation against the loss of heat. The temperature was seen to rise, attain a maximum, remain steady for a few seconds, and then recede. During all this period the distillation of aniline continued, subsiding, however, with the fall of the temperature. This maximum obviously represents the temperature attained by the charge during the optimum reduction to aniline. It was, however, not found identical in different experiments and even with the same mixture it showed good variations, evidently being caused by the differences in the compression, draft of the wind, timing of the heating, etc. Results of different experiments gave 183° as the mean value. Considering the loss of heat sustained by the charge, it is obvious that the optimum temperature will be somewhat higher, 200° representing the ideal temperature because of the facts that it is far below the temperature at which sulphur and $Ca(OH)_2$ begin to react effectively (vide this *Journal*, 1952, **29**, 101) and that it is practically the highest at which nitrobenzene does not begin to distil freely.

DISCUSSION

Results of the qualitative tests given above indicate that nitrobenzene being led over a heated mixture of lime and carbon is not affected in any way, whereas the same treatment with lime-sulphur mixture transforms it into various reduction

products. The stage of reduction depends on the concentration of sulphur in the mixture. When the same is high, more than 33%, the reduction proceeds mainly to the partial stage (Table I, expts. a & b), the nature of which remains to be studied in a later communication. With lowering in the sulphur ratio the formation of aniline gains greater prominence, and with 20% of sulphur in the mixture, this seems to be the only product of the reduction, accompanied, however, with some ammonia. The latter appears to be produced in increasing quantities with the rise in the lime concentration, and is obviously a product from the decomposition of aniline, caused by the heated mass of the base, as, in general, is known to produce such effects (Schulze, *Z. anal. Chem.*, 1867, **6**, 374).

Quantitative estimations (Table II) show that the yield of aniline increases with the rise in the net quantity of sulphur taken in the reaction mixture, and with an weight of the latter almost equal to that of nitrobenzene treated, the same is about 54.0%. Possibly a larger yield can be obtained using a higher proportions of sulphur. Necessitating, however, the addition of a corresponding increased quantity of lime, the mixture was found unwieldy to be treated in such small-scale experiments. Experiments in connection with the determination of the reaction temperature clearly indicate the reaction to be exothermic; and in any case of large scale working, a system of cooling will have to be introduced to keep the temperature down to about 200°, the highest limit wherein reduction of nitrobenzene by lime-sulphur mixture seems to be carried out with best of advantages.

It has been noticed that, when the evolution of H_2S is brisk, as with a high concentration of sulphur in the mixture or with the elevation of the reaction temperature, the formation of aniline is hampered. This, however, is found to be favoured with rather an increased concentration of lime, wherein the chance of the free existence of H_2S is lower. It is thus evident that the reduction of nitrobenzene, in the process under discussion, can hardly be due to the action of H_2S. It is indeed difficult to explain this reduction as also of sulphur found to occur simultaneously except as the work of nascent hydrogen. The precise manner of this mechanism remains to be discussed in a later communication together with the consideration of the cause of the general reducing property possessed by mixtures of dry alkaline earth hydroxides with several non-metallic elements.

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DYES DERIVED FROM ACETONE DICARBOXYLIC ACID

By S. S. Baijal and J. D. Tewari

Acetone dicarboxylic acid has been condensed with resorcinol at 200°. A red crystalline dye (dye I) is obtained which gives a red colour with greenish fluorescence when dissolved in alkali.

A study of the constitution of dye I has been made. A new dye (dye II) has been obtained from 7-hydroxycoumarin-4-acetic acid and resorcinol, and its constitution assigned. The octa- and hexabromo compounds of dyes I and II respectively have also been prepared and studied.

Acetone dicarboxylic acid was condensed with resorcinol by Pechmann (*Annalen*, 1894, **261**, 166) using concentrated sulphuric acid as condensing agent to yield 7-hydroxycoumarin-4-acetic acid.

Later Limaye and Bhave (this *Journal*, 1931, **8**, 137) obtained β-arylglutaconic acids by condensing acetone dicarboxylic acids with phenol using sulphuric acid as a condensing agent at a low temperature.

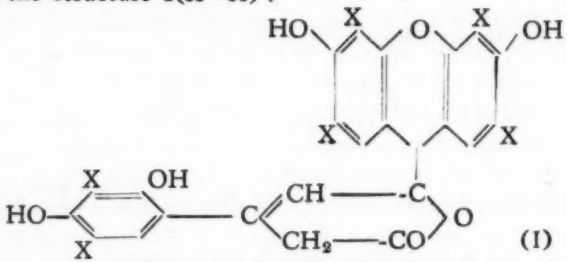
Dixit *et al.* (*ibid.*, 1945, **23**, 207) obtained a dilactone of $\beta\beta$-di-(2 : 4-dihydroxyphenyl)glutaric acid using phosphorus pentoxide or anhydrous aluminium chloride as the condensing agent when acetone dicarboxylic acid was condensed with resorcinol ; Dixit and Mulay (*Proc. Ind. Acad. Sci.*, 1948, **27A**, 14) obtained β-arylglutaconic acid with sulphuryl chloride as a condensing agent.

In the present investigation, acetone dicarboxylic acid was condensed with resorcinol at a high temperature (180-°-200°) using a few drops of concentrated sulphuric acid as the condensing agent. In spite of partial decomposition of the former the product (m. p. 210°) was obtained in good yield. (This resorcinolacetone dicarboxylein will be known hereafter as dye I). Dye I did not react with phenylhydrazine, hydroxylamine etc. indicating the absence of a free carbonyl group.

To understand the mechanism of this condensation, 7-hydroxycoumarin-4-acetic acid, which might be the first product formed, was condensed with resorcinol, but a different compound was obtained which gave a red colour with blue fluorescence when dissolved in alkali. It melted at 179° [this resorcinol-β-(2 : 4-dihydroxyphenyl)-glutaconein will be known hereafter as dye II).

On bromination dye II gave a hexabromo compound. It was supposed that the double bond did not get brominated as on bromination of phenylglutaconein only four atoms of bromine entered the molecule and not six.

The analytical data and the above observation clearly indicate that the dye II has the structure I(X=H) :

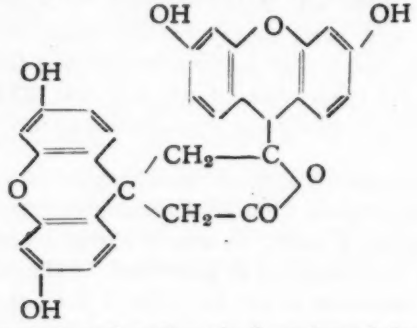


(I)

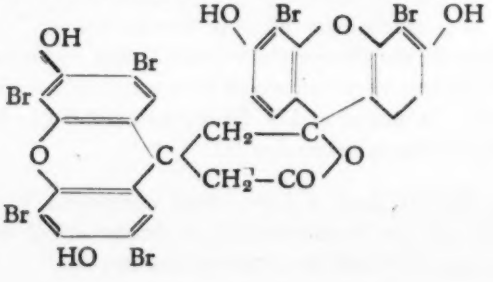
Also the bromo compound of the dye II has been shown to have the structure (I, X=Br).

The formation of the dye II was further confirmed by condensing β-(2 : 4-dihydroxyphenyl)glutaconic acid (Dixit and Mulay, *loc. cit.*) with resorcinol when a dye, identical with dye II, was obtained. Mixed melting point of the two dyes showed no depression.

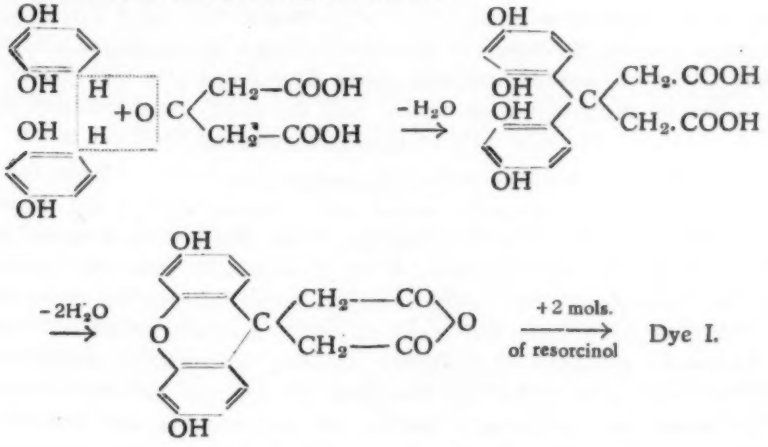
To elucidate the structure of dye I, the dilactone of ββ-di-(2 : 4-dihydroxyphenyl)glutaric acid was condensed with resorcinol at 180°. The product was a mixture, but the pure dye (m. p. 210°) could be obtained, which was found to be identical with dye I (mixed m. p. with dye I). Also the brominated compound of this dye gave the same melting point as the octabromo compound of dye I and showed no depression when their mixed melting point was determined. Dye I on bromination took up eight atoms of bromine, thus, clearly indicating the presence of four aromatic nuclei in dye I. The structure thus assigned to dye I is :



The following formula is assigned to the brominated dye I :



The reaction proceeds probably as follows :



EXPERIMENTAL

Acetone dicarboxylic acid was prepared in the manner as described in "Organic Syntheses" (Coll. Vol. I).

Resorcinol-acetone Dicarboxylein.—An intimate mixture of pure acetone dicarboxylic acid (15 g.) and resorcinol (45 g.) was heated in an oil-bath to 140° ; 4 to 5 drops of concentrated sulphuric acid were then added when a vigorous reaction took place which subsided in 20 to 30 minutes. The temperature was then raised to 200° and the mixture heated for ten hours. On cooling the hard brittle mass was dissolved in a very dilute caustic soda solution, stirred mechanically and to it dilute hydrochloric acid added cautiously. While adding the acid a tarry mass appeared which was removed by filtration before further addition of the acid (if on further addition of the acid a black tarry mass again appears it is to be removed before finally acidifying it). A red dye was obtained which was purified by again dissolving it in caustic soda and precipitating with dilute hydrochloric acid. It was finally purified by dissolving it in dilute alcohol (65% to 70) and diluting with water till a red crystalline dye appeared which was filtered. (The filtrate still contained a mixture of dyes from which the pure dye could not be isolated). It was recrystallised from dilute alcohol. It is a red crystalline substance and gives a beautiful red colour when dissolved in alcohol and a greenish fluorescence on the addition of alkali, m. p. 210°, yield 6 g. (pure). (Found : C, 70.0 ; H, 4.24. $C_{29}H_{20}O_8$ requires C, 70.10 ; H, 4.03 per cent).

Resorcinol-acetone Dicarboxylein from the Dilactone of ββ-di-(2 : 4-dihydroxyphenyl)glutaric Acid.—A mixture of the dilactone (5 g.) and resorcinol (3.5 g.) was heated in an oil bath with a few drops of concentrated sulphuric acid at 180° for 6 hours. It was cooled and extracted with a dilute caustic soda solution and precipitated with dilute HCl. The red dye was repeatedly crystallised from alcohol till a crystalline substance melting at 210° was obtained, yield 0.5 g.

Octabromoresorcinol-acetone Dicarboxylein.—The pure dye (1.2 g.) was dissolved in alcohol or glacial acetic acid and 1 c. c. of bromine slowly added. (If glacial acetic acid is used, a solution of bromine in it is taken). Soon the crystalline dye separated and it was filtered off, washed first with dilute alcohol and then with water. It was further purified by recrystallisation from alcohol and dried under vacuum, m p. 190°, yield 1.8 g. (Found : Br, 56.30. $C_{29}H_{12}O_8Br_8$ requires Br, 56.70 per cent).

Resorcinol-β-(2 : 4-dihydroxyphenyl)glutaconein.—Pure 7-hydroxycoumarin-4-acetic acid (5 g.) was intimately mixed with resorcinol (5 g.) and heated in an oil-bath at 170° for about half an hour and then a few drops of concentrated sulphuric acid were added. A vigorous reaction took place and after the reaction had subsided the temperature was raised to 200°. After heating for about 6 hours it was cooled. The hard mass was extracted with several portions of very dilute sodium hydroxide solution. The alkaline solution was stirred mechanically and dilute hydrochloric acid added very slowly till the solution became acid to litmus. A red dye mixed with some tarry matter was obtained. It was filtered and the crude dye was once more dissolved in dilute caustic soda and reprecipitated cautiously with dilute hydrochloric acid. It was further purified by dissolving in alcohol and diluting the alcoholic solution with water. The dye so obtained was sufficiently pure. Its crystals are red and dissolve in alcohol giving a red colour and a blue fluorescence when alkali is added to it, m. p. 179°, yield : 2 g. (pure dye). (Found : C, 68.30 ; H, 4.50. $C_{23}H_{16}O_7$ requires C, 68.30 ; H, 4.00 per cent).

Resorcinol-β-(2:4-dihydroxyphenyl)-glutaconein from β-(2 : 4-Dihydroxyphenyl)-glutaconic Acid.—An intimate mixture of the acid and resorcinol (2 g. each) was heated in an oil-bath with a few drops of sulphuric acid at 200° for about 6 hours. It was extracted with dilute caustic soda solution and precipitated with dilute hydrochloric acid and finally recrystallised from alcohol, m p. 179°, yield 1 g.

Hexabromoresorcinol-β-(2 : 4-dihydroxyphenyl)-glutaconein.—To the pure resorcinol dye (1 g.), dissolved in the minimum quantity of alcohol, bromine (1.2 c. c.) was added slowly. It was allowed to cool and a few drops of water were added to facilitate the separation of the compound. It was filtered and washed first with very dilute alcohol and then with water till the filtrate was free from bromine. The dye was dried under vacuum. It was purified by recrystallising from alcohol as a dark red crystalline substance, m. p. 243°, yield 1.5 g. It dissolves in alcohol giving a deep red solution, the colour of which is intensified by the addition of alkali. (Found : Br, 54.10. $C_{23}H_{10}O_7Br_6$ requires Br, 54.60 per cent).

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A NOTE ON RAPID ALKALIMETRIC ESTIMATION OF MAGNESIUM, PRESENT ALONE OR IN PRESENCE OF CALCIUM, STRONTIUM, BARIUM AND IN SEA WATER

By Mahadeo M. Tillu

Magnesium is estimated using sodium thiosulphate as a reagent after precipitating it as magnesium hydroxide using either sodium hydroxide, baryta water, strontium hydroxide or lime water as a precipitant. Using the last three precipitants, magnesium can be estimated in presence of barium, strontium and calcium respectively. Further, magnesium can be estimated in presence of all the three alkaline earth radicals and in sea water by using lime water as the precipitant.

Magnesium hydroxide reacts with sodium thiosulphate in the cold forming a double salt, $Na_2Mg(S_2O_3)_2$, disengaging an equivalent amount of alkali which can be titrated. A slight excess of sodium thiosulphate does not interfere with the titration of the alkali. The equation may be represented as

$$Mg(OH)_2+2Na_2S_2O_3 \longrightarrow Na_2[Mg(S_2O_3)_2]+2\ NaOH$$

An aliquot part of magnesium chloride solution was taken in a 100 c. c. flask and an excess of carbonate-free lime water was added, which precipitated magnesium hydroxide completely. The mixture of magnesium hydroxide together with the excess alkali was made up to 100 c. c. with distilled water. It was then vigorously shaken for about 10 minutes and filtered through a dry and neutral filter paper (Whatman No. 44), specially prepared for this purpose by washing the original filter paper at least four times and drying. The funnel, the receiver and the pipette used for the subsequent operations were clean and dry.

The filtrate (50 c. c.) was titrated with $N/10$-HCl, using methyl orange indicator and hence the total excess alkali in 100 c. c. mixture was calculated.

To the remaining filtrate, the filter paper along with the residue was transferred and also the washings of 100 c. c. flask, the funnel and the pipette, used for withdrawing 50 c. c. of the filtrate. Care was taken to carry out all the washings with redistilled water. A carefully neutralised, concentrated solution of sodium thiosulphate was added to the mixture. Sodium thiosulphate reacted with magnesium hydroxide and disengaged an equivalent amount of alkali. The total alkali in the solution was found out by titrating with decinormal hydrochloric acid, using methyl orange indicator.

The excess of the alkali in the mixture being known, the alkali disengaged in the reaction was computed, and hence the amount of magnesium oxide in stock solution calculated. Further, magnesium was estimated in presence of calcium, strontium and barium respectively. The results are shown in Table I. Mean of at least three readings was taken in all the experiments.

TABLE I

Expt. No.	CaO taken.	SrO taken.	BaO taken.	Magnesium oxide taken.	Magnesium oxide found. g	Error Diff.	Error
1	—	—	—	0.009698 g.	0.009697	-0.001 mg.	-0.01%
2	—	—	—	0.01939	0.01935	-0.04	-0 20
3	0.004 g.	—	—	0.01939	0.01935	-0.04	-0.20
4	0.004	—	—	0.009698	0.009676	-0.022	-0.22
5	0.008	—	—	0.009698	0.009676	-0.022	-0.22
6	0.008	—	—	0.01939	0.01945	+0.06	+0.30
7	0.0016	0.004 g.	0.0016 g.	0.01939	0.01945	+0.06	+0.30
8	0.0024	0.006	0.0024	0.01939	0.01941	+0.02	+0.10
9	0.0016	0.004	0.0016	0.009698	0.009780	+0.82	+0.80
10	0.0024	0.006	0.0024	0.009698	0.009724	+0.026	+0.26

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